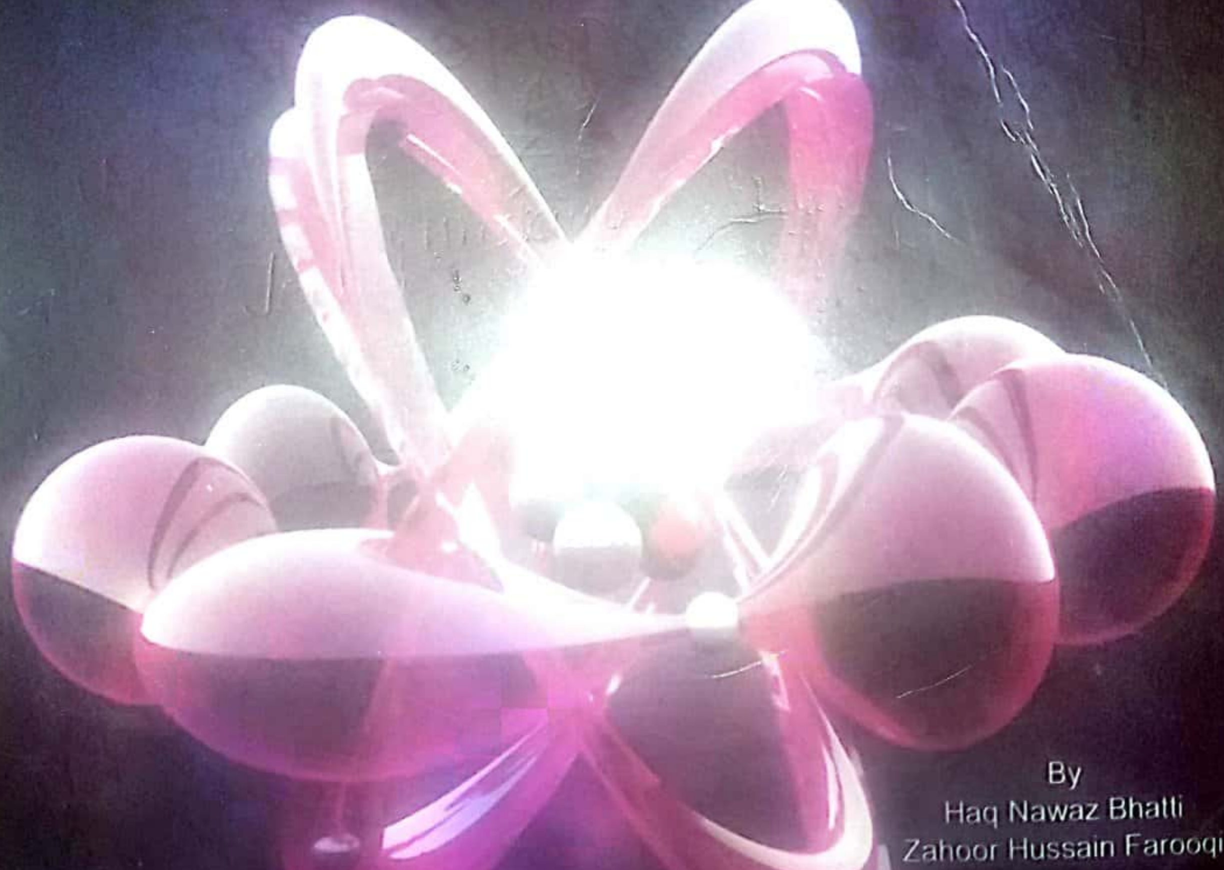
Caravan

Modern
Physical Chemistry

For:
BS and M.Sc Students



By
Haq Nawaz Bhatti
Zahoor Hussain Farooqi

Caravan Book House - Lahore

Modern Physical Chemistry

For:
B.S. and M.Sc. students

Imran Danish

Imran Danish
MSc Chemistry (M)

2019- 2021

mcf 1902045

By
PROF. DR. HAQ NAWAZ BHATTI
MSc (Pb) Gold Medalist
PhD (UAF), Postdoc (Canada)
Fellow PAS, Fellow CSP
Department of Chemistry
University of Agriculture, Faisalabad

DR. ZAHOOR HUSSAIN FAROOQI
MSc (Pb), MPhil & PhD (QAU)
Assistant Professor
Institute of Chemistry
University of The Punjab, Lahore

THE CARAVAN BOOK HOUSE
Kachehri Road, Anarkali Lahore. Phones: 042 37212091, 37212093, 37122955, 37352296
e-mail: caravanbookslhr@gmail.com

Contact:-
0309-7439836.

Title:	Modern Physical Chemistry for B.S. and M.Sc. Students
Authosr:	Dr. Haq Nawaz Bhatti Dr. Zahoor Hussain Farooqi
Published by:	Ch. Ahmad Najib
Printed by:	Bukhari Press Lahore.
Price:	**Rs. 1100/-**

Disclaimer. *Due care and diligence has been taken in compilation and printing of this book, which is being published and sold without any legal and other liability or responsibility on the part of author / publishers / composer / printers for any mistake, misdescription or omission etc.*

All rights reserved under the Copyright Act. No part of this book may be reproduced in any form or by any means, electronic or mechanical, including photocopying, without permission in writing from the author and the publisher. All inquiries should be addressed to the publisher.

PREFACE TO CURRENT EDITION

In recent years the teaching curriculum of Physical Chemistry in many Pakistani Universities has been reconstructed with a great emphasis on a theoretical and conceptual methodology and the applications of the underlying basic concepts and principles. This shift in the emphasis, as we have observed, has unduly frightened the undergraduates and postgraduates whose performance in Physical Chemistry has been otherwise generally far from satisfactory. This poor performance is partly because of the non-availability of a comprehensive textbook which also lays adequate stress on the logical deduction and solution of numerical and related problems. Naturally, the students find themselves unduly constrained when they are forced to refer to various books to collect the necessary reading materials. It is primarily to help these students that we have ventured to present a textbook which provides a systematic and comprehensive coverage of the theory as well as of illustration of the applications.

The field of Physical Chemistry has now become so broad that it has invaded all the sciences. We have tried to write this book in such a way that it will be a useful introduction not only for the students who intend to become Physical Chemists but also for many other students who will find knowledge of Physical Chemistry essential in their careers. The text material of this book is based on the literature to which we were exposed initially while a student and later as a teacher. We have made every effort to write a text suitable for both undergraduates and postgraduates. We have been at some pains to include as much recent material as is feasible in a book at this level without making the book unreasonably long or difficult to follow. Our principal objective has been to present the fundamentals of the subject as clearly as possible.

The students for which the book is intended are assumed to have a basic knowledge of chemistry, physics and calculus. The book is intended primarily for the conventional full year BS/postgraduate courses in Physical Chemistry. However, it covers more than can be included in one-year course; it may therefore be useful in more advanced courses and a general reference book.The book has been written in a simple and lucid style. As it is difficult to cite the sources of information at each appropriate place in the text, we have included a general Bibliography at the end of each chapter. It may however, be remarked that the Bibliography included here reflect only those references which the authors found useful and interesting.

Finally we wish to record our thanks to **Ch. Ahmad Najeeb** for giving open offer to publish this book. Comments and suggestions from the readers will be thankfully acknowledged and incorporated in subsequent editions.

September, 2019, Lahore AUTHORS

Chapter 5 CHEMICAL KINETICS 301
5.1 Introduction 301
5.2 Rate of reaction 301
5.3 Factors affecting the rate of reaction 305
5.4 Rate law and order of reaction 305
5.5 Zero order reaction 307
5.6 First order reaction 309
5.7 Second order reaction 321
5.8 Third order reaction 327
5.9 Opposing reaction 339
5.10 Parallel reactions 367
5.11 Consecutive reaction 377
5.12 Methods for the determination of order of a reaction 390
5.13 Kinetics and reaction mechanism 398
5.14 Unimolecular gas phase reaction 409
5.15 Basic experimental methods of kinetics 414
5.16 Effect of temperature on the rate of a reaction 434
5.17 Theories of reaction rates 438
5.18 Reactions in solutions 448

Chapter 6 SURFACE CHEMISTRY 465
6.1 Introduction 465
6.2 Adsorption 465
6.3 Factors affecting adsorption 466
6.4 Adsorption isotherms 467
6.5 Langmuir adsorption isotherm for adsorption of single gas system 470
6.6 Application of Langmuir adsorption isotherm for single system 478
6.7 Langmuir adsorption isotherm for double system 491
6.8 Catalytic reaction of two gases on solid surface 495
6.9 Catalytic inorganic reactions 503
6.10 Catalysis or use of catalyst in industry 507
6.11 Advanced approach to homogeneous catalysis 509
6.12 Enzyme inhibition 525
6.13 B.E.T Equation 536
6.14 Surface Area Determination of Solid Adsorbents 543

Chapter 7 NUCLEAR CHEMISTRY 549
7.1 Introduction 549
7.2 The atom 550
7.3 The atomic nucleus 550
7.4 Composition of nucleus 552
7.5 Properties of the nucleus 553

7.6 The fundamental particles 554
7.7 Nuclear stability 556
7.8 Nuclear terms 559
7.9 Nuclear energetic 561
7.10 Nuclear models 566
7.11 Radioactivity 568
7.12 Detection and measurement of radioactivity 571
7.13 Interaction of ionizing radiation with matter 575
7.14 Radiation dosimetery 577
7.15 Radioactive decay 580
7.16 Kinetics of radioactive decay 585
7.17 Half Life and Decay Constant 587
7.18 Average or mean life 590
7.19 Theory of radioactive disintegration 592
7.20 Artificial or induced radioactivity 595
7.21 Successive radioactive and radioactive equilibrium 597
7.22 Nuclear reactions 601
7.23 Nuclear fission 603
7.24 The atomic bomb 605
7.25 Nuclear fusion and Stellar energy 606
7.26 Hydrogen bomb 608
7.27 Nuclear reactor 609
7.28 Charged particles accelerators 611
7.29 Radiation hazards and safety measures 615
7.30 Applications of tracers in chemistry 618

Chapter 8 MOLECULAR SYMMETRY 627
8.1 Introduction 627
8.2 Defining the coordinate system 628
8.3 Symmetry elements and symmetry operations 629
8.4 Identity element 630
8.5 Proper axis of symmetry 630
8.6 The reflection operation and mirror plane 634
8.7 Rotation-reflection and the improper axis 636
8.8 The inversion operation and the centre of symmetry 638
8.9 The symmetry point groups 640
8.10 Multiplication of symmetry operators 648
8.11 Optical activity and dipole moments on basis of point group symmetry 651
8.12 Order of a Group 652
8.13 Similarity Transformation 652
8.14 Class of a Group 653
8.15 Matrices 654

8.16 Matrix Representations of Symmetry Operations 659
8.17 Symmetry Properties of Atomic Orbitals 663
8.18 Reducible and Irreducible Representations 665
8.19 Generation of an Irreducible Representation 668
8.20 Generation of Reproducible Representation 670
8.21 Character Tables for Point Groups 672
8.22 Great Orthogonality Theorem 673
8.23 Construction of Character Tables for Point Groups 675
8.24 Decomposition of Reducible Representations 676

Chapter 9 ELECTROCHEMISTRY 683
9.1 Introduction 683
9.2 Conductors and insulators 684
9.3 Ohm's Law and electrical units 685
9.4 Electrolytic conductance 686
9.5 Equivalent and molar conductance 688
9.6 Measurement of conductance 689
9.7 Cell constant 692
9.8 Variation of conductance with concentration 694
9.9 Effect of temperature on the conductance 696
9.10 Effect of dielectric constant of the solvent on conductance 697
9.11 Effect of viscosity on conductance 697
9.12 Arrhenius Theory of electrolytic dissociation 698
9.13 The Ostwald's Dilution law 699
9.14 Theory of strong electrolytes 702
9.15 Debye-Huckel Theory: The ionic atmosphere 704
9.16 Debye-Huckel-Onsager's Eequation 710
9.17 Wein and Debye-Falkenhagen effects 715
9.18 Ionic strength 716
9.19 Activities and activity coefficients of strong electrolytes 718
9.20 Debye-Huckel limiting law 722
9.21 Determination of activity coefficients of electrolytes 727

Chapter 10 ELECTROCHEMICAL CELLS 737
10.1 Introduction 737
10.2 Types of electrochemical cells 737
10.3 Electrode reactions and concept of half cell 740
10.4 Reversible and irreversible cells 740
10.5 Types of reversible electrodes 741
10.6 Electromotive force and its measurement 744
10.7 Electrode potential 746
10.8 Cell potential (Ecell) 752

10.9 Electrochemical conventions and notations 755
10.10 Thermodynamic aspects of cell potential 757
10.11 Thermodynamics of electrode potential-Nernst equation 761
10.12 Concentration cells 762
10.13 Liquid junction potential 768
10.14 Fuel cells 771
10.15 Voltammetry 775
10.16 Fuel Cells 778
10.17 Corrosion and its Prevention 781

Chapter 11 EMULSIONS AND GELS 787
11.1 Introduction 787
11.2 Surface Tension 788
11.3 Interfacial Tension and Spreading of Liquids 789
11.4 Pressure Drop Across a Curved Surface or Curved Interfaces 793
11.5 Vapour Pressure Along Curved Surface: Kelvin Equation 794
11.7 Colloidal System 796
11.8 Emulsion 797
11.9 Characterization of Simple Emulsion 800
11.10 Surfactants: Emulsifiers 804
11.11 Properties of Surfactants 805
11.12 Gibbs's Adsorption Equation 807
11.13 Critical Micelle Concentration 809
11.14 Micellization of Non-Ionic Surfactant 811
11.15 Thermodynamics of Micellization 812
11.16 Techniques Used to Study Micellization Parameters 815
11.17 Theories of Emulsion Type 819
11.18 Stability of Emulsion 824
11.19 Breaking of Emulsion (Demulsification) 824
11.20 Methods of Emulsion Preparation 827
11.21 Applications of Emulsions 830
11.22 Gels 832
11.23 Methods for the Preparation of Gels 836
11.24 Properties of Gels 838
11.25 Applications of Gels 841

Chapter 12 PHOTOCHEMISTRY 847
12.1 Introduction 847
12.2 Photochemical and thermal reactions 848
12.3 Light absorption and Beer-Lambert law 848
12.4 Laws of photochemistry 856
12.5 Quantum Yield and its Experimental Determination 860

12.6 Photophysical processes 862

12.7 Non radiative relaxation processes 863

12.8 Radiative relaxation processes 863

12.9 Quantitative aspects of fluorescence 865

12.10 Kinetic aspects of phosphorescence 873

12.11 The photochemical reaction between bromine and hydrogen 878

12.12 The photochemical reaction between hydrogen and chlorine 881

12.13 Photochemical Decomposition of Acetaldehyde 884

12.14 Photochemical Decomposition of Acetaldehyde 884

12.15 Flash Photolysis 886

12.16 Chemiluminescence 887

12.17 Photosensitized reaction 888

12.18 Lasers 889

12.19 Photochemistry of Vision 894

Chapter 13 POLYMER CHEMISTRY 899

13.1 Introduction 899

13.2 Classification of Polymers 900

13.3 Polymerization 905

13.4 Step Growth Polymerization 905

13.5 Chain Growth Polymerization 915

13.6 Copolymerization 934

13.7 Molecular Weight Averages 942

13.8 Molecular Mass Determination Methods 947

13.9 Analytical Method 959

Appendices 963

Chapter 6

SURFACE CHEMISTRY

6.1 INTRODUCTION

Surface chemistry is the branch of physical chemistry which deals with the study of phenomena occurring at interfaces. The study of interfaces is of great significance for chemists because it finds applications in our daily life and industry. Mainly, surfaces play an important role in catalysis, colloid formation, chromatography etc. This chapter covers the fundamentals and applications of surface chemistry. Adsorption is the process of attachment of adsorbate molecules on the surface of adsorbent. This chapter explains the adsorption isotherms, adsorption of a gas and its catalytic reaction on solid surface. Adsorption of two gases and their catalytic reaction on solid surface and retardation process is also explained with the help of Langmuir adsorption isotherm. Eley-Rideal mechanism and Langmuir-Hinshelwood mechanisms to study some organic and inorganic reactions have been described in this chapter. Catalytic decomposition of ammonia is also described by the Tempkin adsorption isotherm in detail. The gas-solid interface is of great importance in catalysis. The current chapter also covers some basic physical aspects of catalysis, autocatalysis, enzyme catalysis and enzyme inhibition. Moreover comparative analysis of competitive, uncompetitive and non-competitive enzyme inhibitions is also discussed in this chapter.

6.2 ADSORPTION

When molecules of a substance come in contact with any solid surface its molecules get attached on it, this process of attachment of molecules is named as adsorption. In other words, *"attachment of particles of a substance on the surface of another substance is called adsorption."* Adsorbate and adsorbent are basic components which are necessary for adsorption. Adsorbate is the substance which get attached to the other surface and the substance on which adsorption takes place is called adsorbent. Adsorption can be distinguished from absorption because in adsorption adsorbate molecules will attach at the surface while in case of absorption, molecules will penetrate into the body of adsorbent. So, *"the penetration of the molecules of a substance into the other substance is called absorption."*

When adsorption and absorption takes place at same time then the process is known as sorption. The dyeing of cotton fibers is an example of sorption.

Types of Adsorption

There are two types of adsorption i.e. physical and chemical adsorption. Some distinguishing characteristics are given below

Physical Adsorption	Chemical Adsorption
1 Physical adsorption occurs through van-der Waal's forces. So, it is also known as physiosorption.	1. Chemical adsorption occurs through chemical bonding. It is also known as chemisorption.
2. Physical adsorption is fast process.	2. Chemical adsorption is slow process.
3. This is relatively weak adsorption.	3. This is relatively strong adsorption.
4. It has low value of heat of adsorption.	4. It has high value of heat of adsorption.
5. Physical adsorption is mostly exothermic process.	5. The process of chemisorption may be exothermic or endothermic.
6. It is not specific.	6. It is highly specific.
7. It depends only on the nature of adsorbate.	7. It depends on the nature of adsorbate and adsorbent.
8. It is usually multilayered adsorption	8. It is monolayered adsorption
9. It decreases with rise of temperature.	9. It increases with increase of temperature.
10. It is reversible process.	10. It may be irreversible or reversible process.
11. Heat of adsorption is less than 40 kJ/mol.	11. Heat of adsorption is greater than 80 kJ/mol.
12. For example, Adsorption of oxalic acid on charcoal.	12. For example, H_2 adsorbed on Ni/Fe/Pt.

6.3 FACTORS AFFECTING ADSORPTION

(i) Nature of Adsorbate and Adsorbent

Adsorption depends upon the nature of adsorbate and adsorbent. The various groups of adsorbate and adsorbent are responsible for adsorption. For example polarity of both can cause force of attraction between them.

(ii) Surface Area

Surface area of the adsorbent has pronounced effect on the rate of adsorption. Adsorbent with greater surface to volume ratio possess greater extent of adsorption and vice versa. If substance is divided and subdivided further then we get small particles. This process will increase the surface area to volume ratio to a very large extent.

(iii) Temperature

Temperature affects the process of adsorption. For example in most cases chemical adsorption increases with the increase of temperature, while physical adsorption decreases with the increase of temperature.

(iv) Pressure/Concentration

Dynamic equilibrium exists between the adsorbed and desorbed gas molecules during adsorption process. So, according to Le-Chatlier's principle increase in pressure leads to higher rate of adsorption. When pressure is decreased it causes desorption.

6.4 ADSORPTION ISOTHERMS

Adsorption of a substance on the surface of another substance can be investigated under various conditions of temperature and pressure but in most studies relation between extent of adsorption and equilibrium pressure has been explored. When a gas starts to adsorb on a surface, initially its rate of desorption depends upon number of molecules adsorbed. With the increase of number of molecules adsorbed, rate of desorption increases. *"When rate of adsorption becomes equal to the rate of desorption this state is called dynamic equilibrium."* At dynamic equilibrium, the pressure is called equilibrium pressure. The process of adsorption and desorption in a close vessel is shown in Fig. 6.1 (a) at equilibrium. *"The relation between extent of adsorption and equilibrium pressure at constant temperature is called adsorption isotherm."*

6.4.1 Freundlich Adsorption Isotherm

Freundlich gave an empirical relation between extent of adsorption and pressure of gas at constant temperature in the form of an empirical equation which is given below

$$\frac{x}{m} = kP^{1/n} \tag{6.1}$$

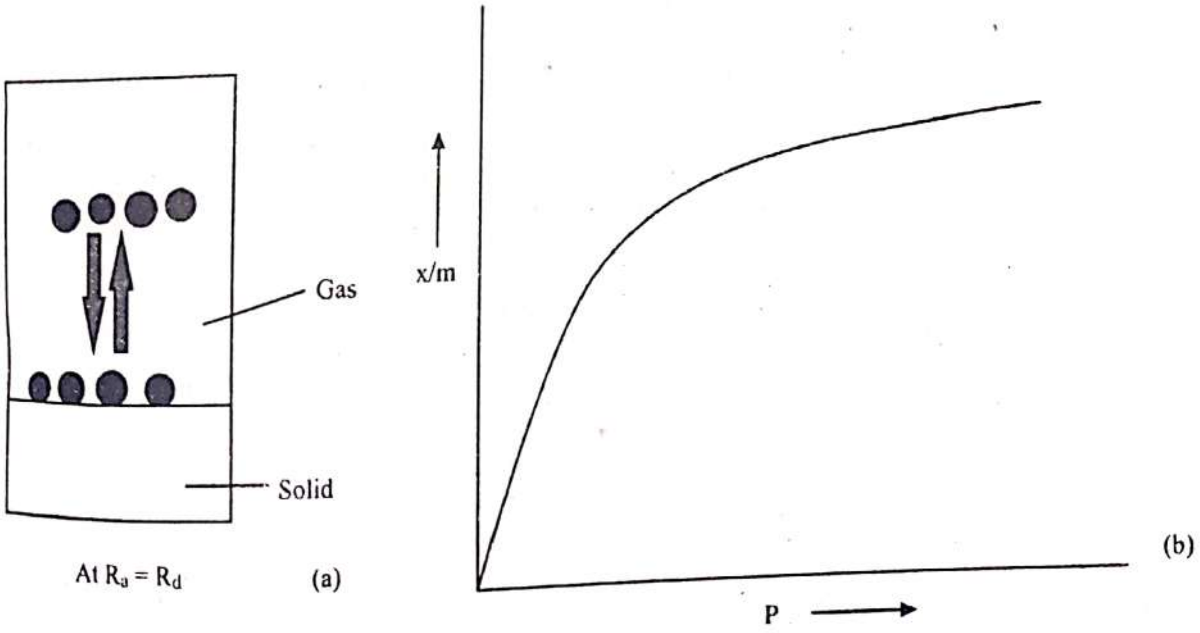


Fig. 6.1 (a) Adsorption desorption equilibrium
(b) x/m as a function of pressure of a gas at constant temperature

Where, P is the equilibrium pressure and x/m is the extent of adsorption i.e. amount of adsorbate adsorbed per unit mass of adsorbent. k and n are empirical constants which depend upon the nature of gas, solid and temperature, n is the dimensionless quantity but k has dimension of inverse of pressure. According to equation (6.1) extent of adsorption is a function of equilibrium pressure of gas as shown in Fig. 6.1 (b).

Equation (6.1) can be written in the form of equation of straight line as

$$\log\frac{x}{m} = \frac{1}{n}\log P + \log k \tag{6.2}$$

According to equation (6.2) log (x/m) is a linear function of logP whose slope and intercept are 1/n and log k respectively as shown in Fig. 6.2. This plot can be used for the determination of values of empirical constants n and k.

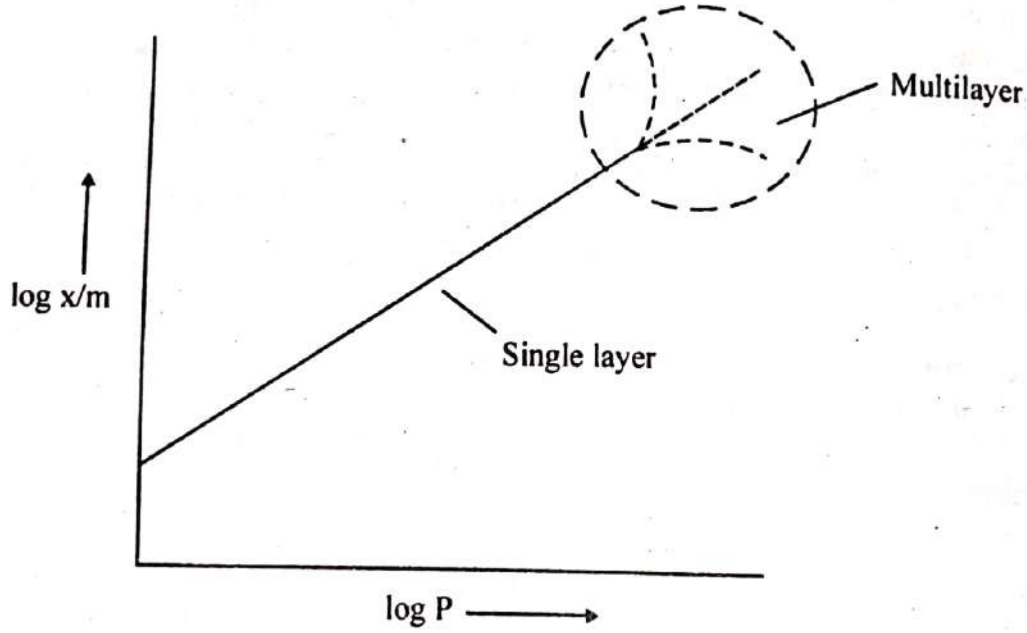


Fig. 6.2 Plot of log x/m versus log P with slight curvature at high pressure

When value of 1/n approaches to zero, then x/m becomes independent of pressure and 1/n approaches to one then x/m becomes a linear function of pressure of gas as shown in Fig. 6.3.

Freundlich adsorption isotherm for adsorption from solution to a solid surface can be written by replacing P with C in equation (6.1) as

$$\frac{x}{m} = kC^{1/n} \tag{6.3}$$

By taking log of equation (6.3)

$$\log\frac{x}{m} = \log k + \frac{1}{n}\log C$$

This equation can be used to study the adsorption of toxic material on biosorbent in aqueous medium. Water purification can be done by suitable adsorbent using this equation. The value of n and k can be determined using plot as shown in Fig. 6.4.

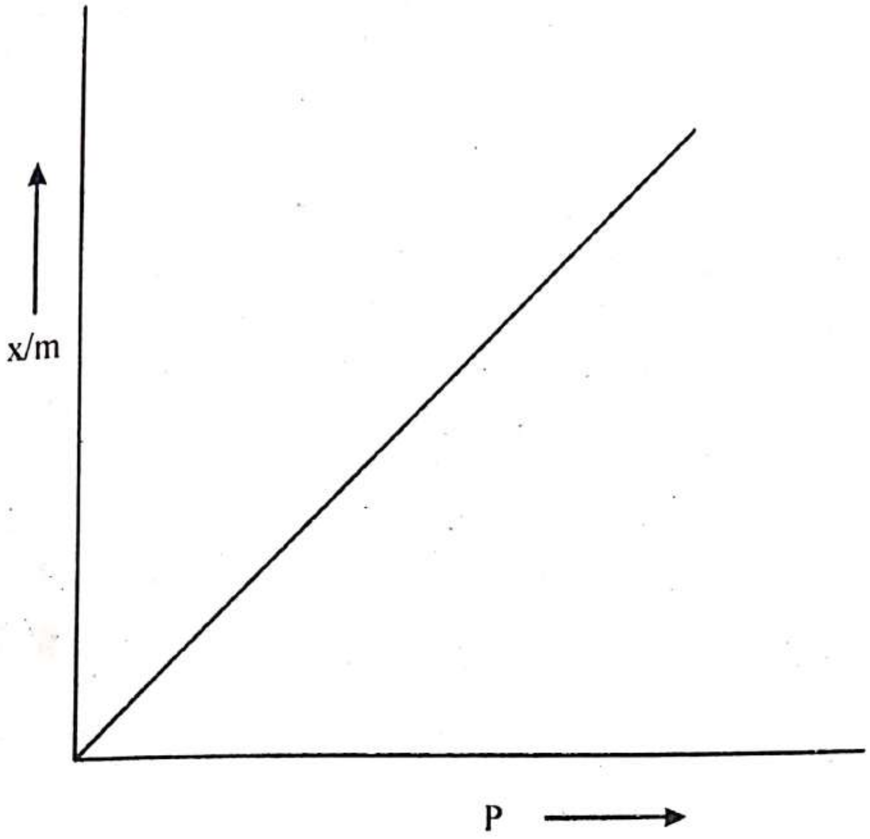


Fig. 6.3 Plot of x/m as a function of pressure when n = 1

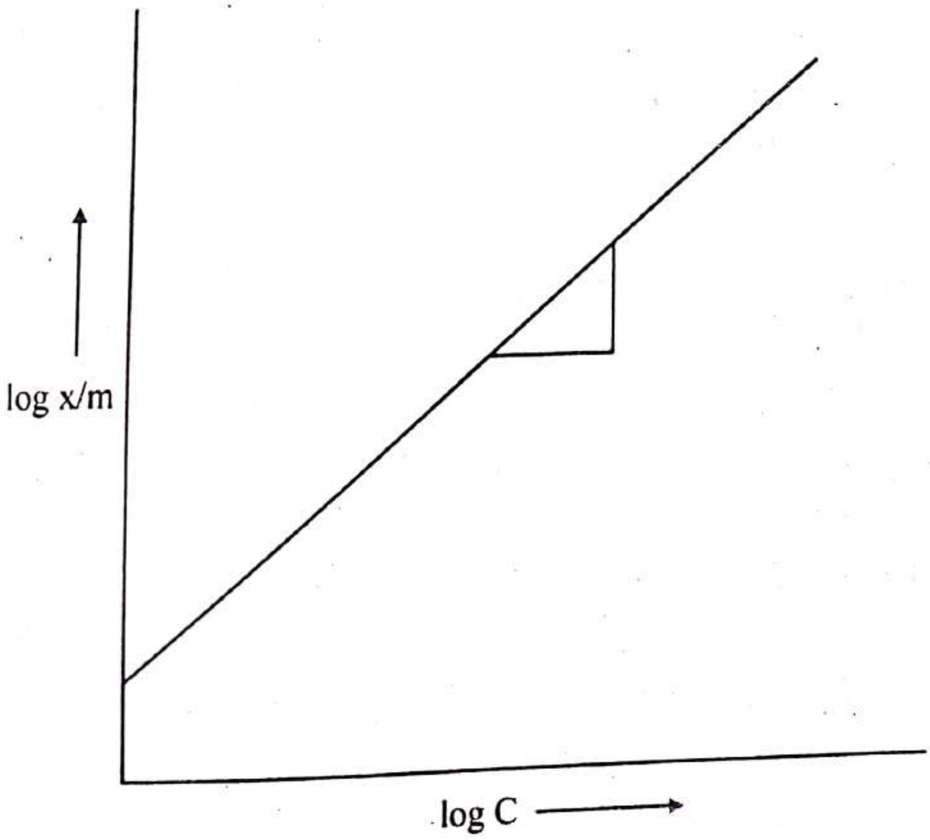


Fig. 6.4 Plot of log x/m versus log C

6.4.2 Langmuir's Adsorption Isotherm

Langmuir was an American physical chemist who worked on adsorption of gases on solid surface. He also derived "adsorption isotherm" and got noble prize in chemistry in 1932. The postulates on which Langmuir's adsorption isotherm is based are given below.

Postulates

(i) Each adsorbent has specific equivalent sites for adsorption.

(ii) Adsorbate molecule attach to these sites.

(iii) One molecule of adsorbate can adsorb on one site of adsorbent.

(iv) There is no interaction between molecules of adsorbate adsorbed.

(v) Rate of adsorption is relatively high as compared to rate of desorption at initial stages.

(vi) Rate of adsorption becomes equal to rate of desorption at dynamic equilibrium as shown in Fig. 6.5.

(vii) Fractional surface coverage (θ), a new dimensionless quantity is equal to the ratio of number of sites covered to total number of sites i.e.

$$\theta = \frac{\text{no. of sites occupied}}{\text{total no. of sites}}$$

(viii) Rate of adsorption depends upon the equilibrium pressure of gas (adsorbate) and fraction of available sites and rate of desorption depends upon the fraction of sites covered.

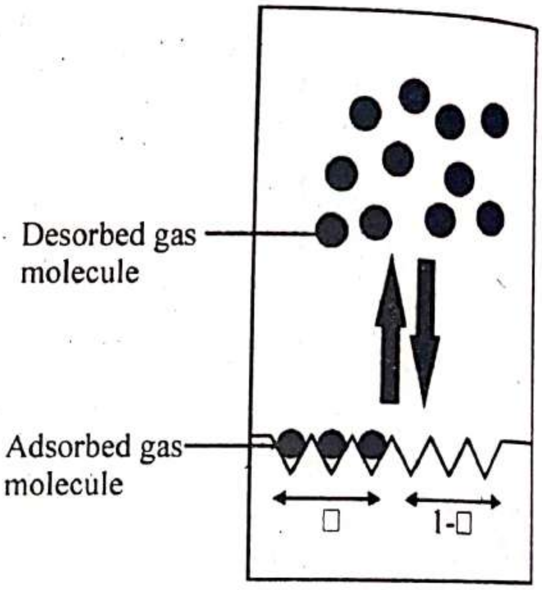


Fig. 6.5 Dynamic equilibrium exists between adsorbed and desorbed molecules

6.5 LANGMUIR ADSORPTION ISOTHERM FOR ADSORPTION OF SINGLE GAS SYSTEM

Adsorption of a gas on solid surface is described by Langmuir adsorption isotherm which is a relation between fractional surface coverage and pressure of gas. The adsorption of a gas on solid surface may be non dissociative and dissociative. The Langmuir adsorption isotherm for both type of adsorption is described here.

6.5.1 Langmuir Adsorption Isotherm for Non Dissociative Adsorption

The adsorption process during which gas molecules adsorbed as such without any dissociation is called non dissociative adsorption. Non dissociative adsorption of hydrogen on a solid surface can be written as

$$H_{2(gas)} \leftrightarrow H_{2(Ads)}$$

Rate of adsorption of a gas is directly proportional to pressure and fraction of unoccupied sites i.e.

$$R_{Ads} \propto P_A \qquad (6.4)$$

$$R_{Ads} \propto (1-\theta) \qquad (6.5)$$

On combining equation (6.4) and (6.5)

$$R_{Ads} = k_{Ads}(1-\theta)P_A \qquad (6.6)$$

$k_{ads.}$ is the rate constant for adsorption.

According to Arrhenius equation k_{ads} is the function of temperature and can be written as $k_{Ads} = b_1 e^{-\frac{E_{Ads}}{RT}}$. Then equation (6.6) will become

$$R_{Ads} = b_1 e^{-\frac{E_{Ads}}{RT}}(1-\theta)P_A \qquad (6.7)$$

Rate of desorption is directly proportional to fractional surface coverage i.e.

$$R_{Des} \propto \theta$$

$$R_{Des} = k_{Des}\theta$$

$$k_{Des} = b_2 e^{-\frac{E_{Des}}{RT}}.\theta \qquad (6.8)$$

At dynamic equilibrium, rate of adsorption becomes equal to the rate of desorption. So,

$$R_{Ads} = R_{Des}$$

By comparing equation (6.7) and (6.8) we get,

$$b_1 e^{-\frac{E_{Ads}}{RT}}(1-\theta)P_A = b_2 e^{-\frac{E_{Des}}{RT}}.\theta$$

$$b_1 e^{-\frac{E_{Ads}}{RT}}P_A - b_1 e^{-\frac{E_{Ads}}{RT}}\theta P_A = b_2 e^{-\frac{E_{Des}}{RT}}.\theta$$

$$b_1 e^{-\frac{E_{Ads}}{RT}}P_A = b_1 e^{-\frac{E_{Ads}}{RT}}\theta P_A + b_2 e^{-\frac{E_{Des}}{RT}}\theta$$

$$b_1 e^{-\frac{E_{Ads}}{RT}}P_A = \theta\left\{b_1 e^{-\frac{E_{Ads}}{RT}}P_A + b_2 e^{-\frac{E_{Des}}{RT}}\right\}$$

$$\theta = \frac{b_1 e^{-\frac{E_{Ads}}{RT}}P_A}{b_2 e^{-\frac{E_{Des}}{RT}} + b_1 e^{-\frac{E_{Ads}}{RT}}P_A}$$

Multiplying and dividing right hand side of equation by $b_2 e^{-\frac{E_{Des}}{RT}}$

$$\theta = \frac{b_1 e^{-\frac{E_{Ads}}{RT}} P_A / b_2 e^{-\frac{E_{Des}}{RT}}}{1 + \dfrac{b_1 e^{-\frac{E_{Ads}}{RT}} . P_A}{b_2 e^{-\frac{E_{Des}}{RT}}}}$$

$$\theta = \frac{\dfrac{b_1}{b_2} e^{\frac{E_{Des}}{RT}} e^{-\frac{E_{Ads}}{RT}} P_A}{1 + \dfrac{b_1}{b_2} e^{\frac{E_{Des}}{RT}} e^{-\frac{E_{Ads}}{RT}} P_A}$$

$$\theta = \frac{\left(\dfrac{b_1}{b_2}\right) e^{\frac{E_{Des} - E_{Ads}}{RT}} P_A}{1 + \left(\dfrac{b_1}{b_2}\right) e^{\frac{E_{Des} - E_{Ads}}{RT}} P_A}$$

$$\theta = \frac{\left(\dfrac{b_1}{b_2}\right) e^{\frac{-(E_{Ads} - E_{Des})}{RT}} P_A}{1 + \left(\dfrac{b_1}{b_2}\right) e^{\frac{-(E_{Ads} - E_{Des})}{RT}} P_A} \qquad (6.9)$$

And, $\Delta H_{Ads} = E_{Ads} - E_{Des}$ (6.10)

The quantity E_{Ads}-E_{Des} is the heat of adsorption as shown in energy profile in Fig. 6.6.

Putting value of (E_{Ads}– E_{Des}) from equation (6.10) into equation (6.9), we get

$$\theta = \frac{\left(\dfrac{b_1}{b_2}\right) e^{-\frac{\Delta H_{Ads}}{RT}} P_A}{1 + \left(\dfrac{b_1}{b_2}\right) e^{-\frac{\Delta H_{Ads}}{RT}} P_A}$$

$$\left(\frac{b_1}{b_2}\right) e^{-\frac{\Delta H_{Ads}}{RT}} = b$$

So, above equation becomes

$$\theta = \frac{bP_A}{1 + bP_A} \qquad (6.11)$$

b is the adsorption coefficient which depends upon the nature of adsorbate and adsorbent, it is temperature dependent and its units are Pa^{-1}.

Equation (6.11) is a relation between fractional surface coverage and pressure of gas. According to equation (6.11) θ is a function of pressure of gas. Fig. 6.7 gives dependence of θ on pressure. The value of θ increases with the increase of pressure of gas for small range of pressure and it becomes independent of pressure at very high value of pressure. At this stage, all sites are occupied by gas molecules, that is why further increase of pressure has no effect on extent of adsorption.

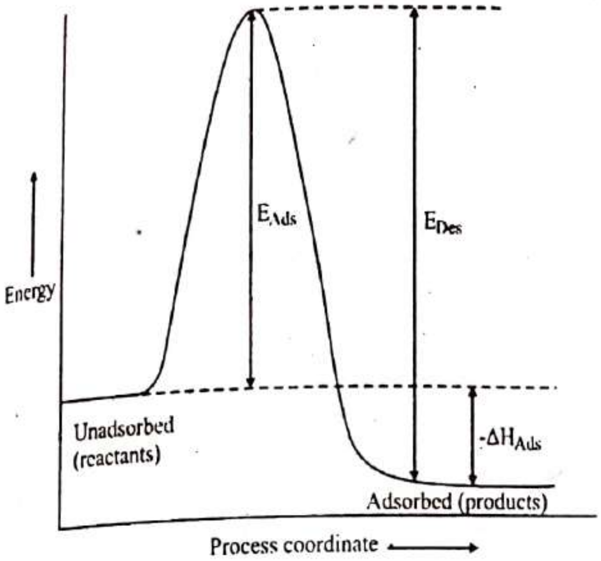


Fig. 6.6 Energy profile of adsorption and desorption processes

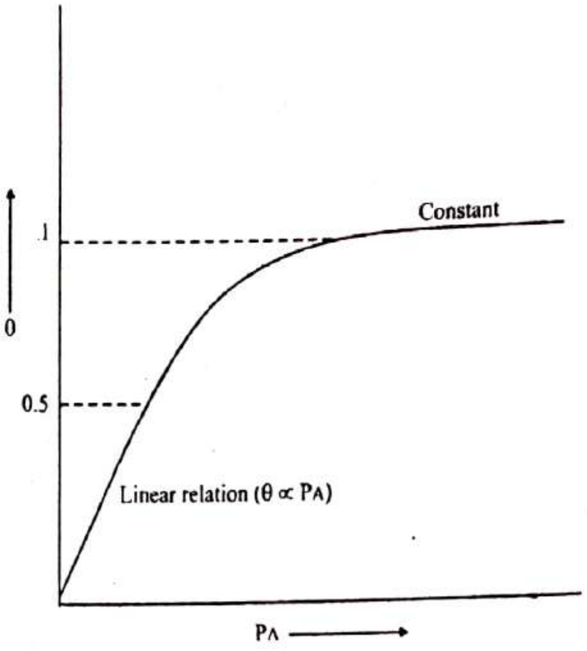


Fig. 6.7 θ as a function of pressure of gas A

Special Cases

(i) When P_A is low, then $1 + bP_A \approx 1$. So, equation (6.11) will become

$$\theta = bP_A$$

$$\theta \propto P_A$$

So, θ is a linear function of P_A.

(ii) When P_A is high, then $1 + bP_A \approx bP_A$. Then, equation (6.11) becomes

$$\theta = 1$$

So, fractional surface coverage is independent of available pressure. At this stage, adsorption or value only depends upon value of b. If weak adsorption occurs, then b has low value and if strong adsorption occurs, then value of b will be high.

By taking inverse of equation (6.11)

$$\frac{1}{\theta} = \frac{1 + bP_A}{bP_A}$$

$$\frac{1}{\theta} = \frac{1}{bP_A} + 1$$

$$\frac{1}{\theta} = \left(\frac{1}{b}\right)\left(\frac{1}{P_A}\right) + 1$$

This is an equation of straight line with intercept 1 and slope 1/b.

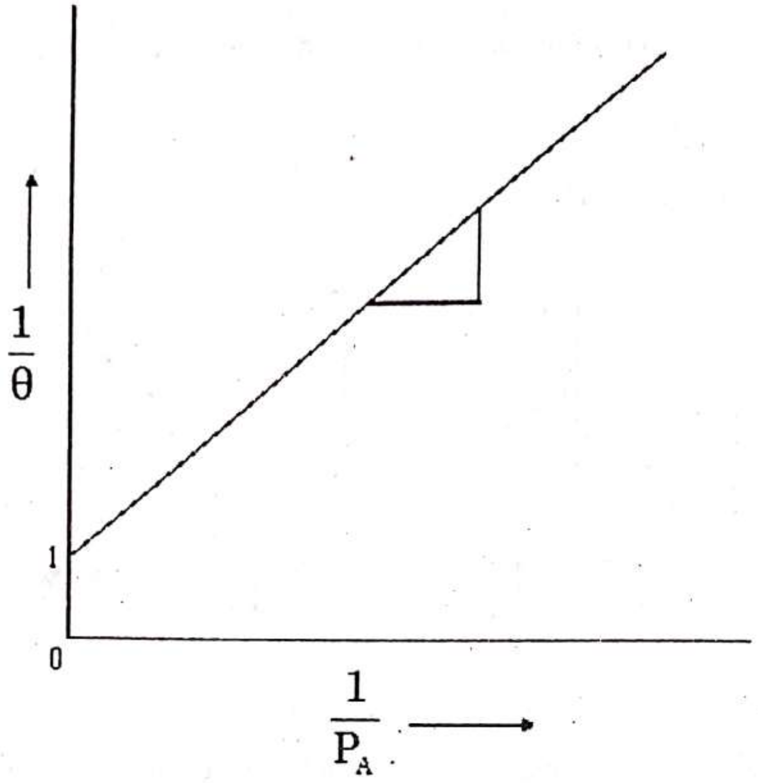


Fig. 6.8 Plot of 1/θ versus 1/P_A

Fig. 6.8 shows that 1/θ is directly proportional to 1/P_A. From the slope of this graph, value of b can be determined.

6.5.2 Langmuir Adsorption Isotherm for Dissociative Adsorption of a gas

The adsorption process during which dissociation of gas molecules takes place is called dissociative adsorption and for dissociative adsorption rate of adsorption is directly proportional to pressure and square of fraction of vacant sites of adsorbent i.e.

$$R_{Ads} \propto (1-\theta)^2$$

$$R_{Ads} \propto P_A$$

On combining above both equations we get,

$$R_{Ads} = k_{Ads}(1-\theta)^2 P_A \qquad (6.12)$$

According to Arrhenius equation: $k_{Ads} = b_1 e^{-\frac{E_{Ads}}{RT}}$

So, equation (6.12) becomes

$$R_{Ads} = b_1 e^{-\frac{E_{Ads}}{RT}} P_A (1-\theta)^2 \qquad (6.13)$$

Rate of desorption is directly proportional to square of fractional surface coverage because two vacant sites are formed when a molecule of desorbed gas formed from adsorbed gas. It means it is second order reaction. Thus

$$R_{Des} \propto \theta^2$$

$$R_{Des} = k_{Des}\theta^2 \tag{6.14}$$

According to Arrhenius equation: $k_{Des} = b_2 e^{-\frac{E_{Des}}{RT}}$

So, equation (6.14) will become

$$R_{Des} = b_2 e^{-\frac{E_{Des}}{RT}}\theta^2 \tag{6.15}$$

E_{Ads} is the energy of activation for adsorption while, E_{Des} is the energy of activation for desorption process.

Initially rate of adsorption is greater than rate of desorption according to Langmuir, but rate of adsorption decreases with the passage of time because number of vacant sites decreases. Rate of desorption increases with time because number of occupied sites increases.

At dynamic equilibrium, rate of adsorption become equal to the rate of desorption as given below

$$R_{Ads} = R_{Des}$$

$$b_1 e^{-\frac{E_{Ads}}{RT}}(1-\theta)^2 P_A = b_2 e^{-\frac{E_{Des}}{RT}}.\theta^2$$

$$b_1^{1/2} e^{-\frac{E_{Ads}}{2RT}}(1-\theta)P_A^{1/2} = b_2^{1/2} e^{-\frac{E_{Des}}{2RT}}.\theta$$

$$b_1^{1/2} e^{-\frac{E_{Ads}}{2RT}}P_A^{1/2} - b_1^{1/2} e^{-\frac{E_{Ads}}{2RT}}\theta P_A^{1/2} = b_2^{1/2} e^{-\frac{E_{Des}}{2RT}}\theta$$

$$b_2^{1/2} e^{-\frac{E_{Des}}{2RT}}\theta + b_1^{1/2} e^{-\frac{E_{Ads}}{2RT}}\theta P_A^{1/2} = b_1^{1/2} e^{-\frac{E_{Ads}}{2RT}}P_A^{1/2}$$

$$\theta\left(b_2^{1/2} e^{-\frac{E_{Des}}{2RT}} + b_1^{1/2} e^{-\frac{E_{Ads}}{2RT}}P_A^{1/2}\right) = b_1^{1/2} e^{-\frac{E_{Ads}}{2RT}}P_A^{1/2}$$

$$\theta = \frac{b_1^{1/2} e^{-\frac{E_{Ads}}{2RT}}P_A^{1/2}}{b_2^{1/2} e^{-\frac{E_{Des}}{2RT}} + b_1^{1/2} e^{-\frac{E_{Ads}}{2RT}}P_A^{1/2}} \tag{6.16}$$

Divide above equation numerator and denominator by $b_2^{1/2} e^{-\frac{E_{Des}}{2RT}}$

$$\theta = \frac{\left(\frac{b_1}{b_2}\right)^{1/2} e^{-\frac{(E_{Ads}-E_{Des})}{2RT}} P_A^{1/2}}{1+\left(\frac{b_1}{b_2}\right)^{1/2} e^{-\frac{(E_{Ads}-E_{Des})}{2RT}} P_A^{1/2}} \tag{6.17}$$

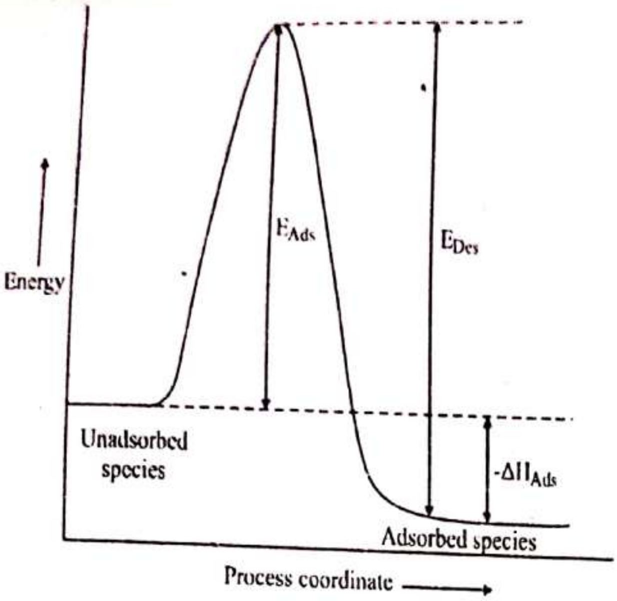


Fig. 6.9 Energy profile of adsorption of a gas

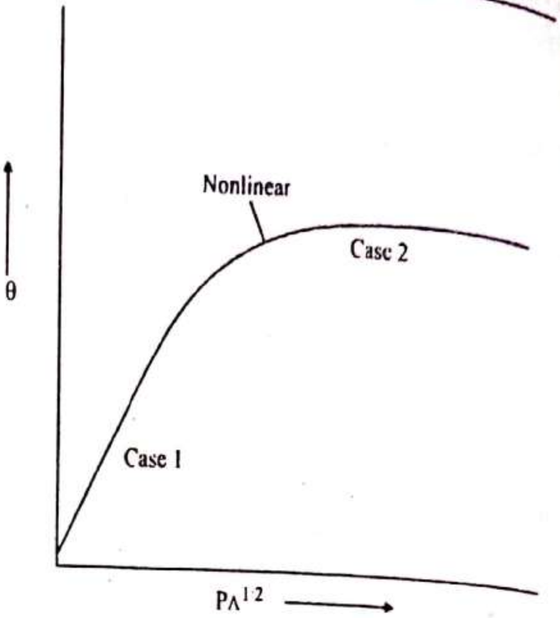


Fig. 6.10 Plot of θ as a function of $P_A^{1/2}$

ΔH_{Ads} denotes enthalpy of adsorption according to Fig. 6.9. ΔH_{Ads} is equal to

$$\Delta H_{Ads} = E_{Ads} - E_{Des} \tag{6.18}$$

Putting value of $(E_{Ads} - E_{Des})$ from equation (6.18) into equation (6.17)

$$\theta = \frac{\left(\frac{b_1}{b_2}\right)^{1/2} e^{-\frac{\Delta H_{Ads}}{2RT}} P_A^{1/2}}{1 + \left(\frac{b_1}{b_2}\right)^{1/2} e^{-\frac{\Delta H_{Ads}}{2RT}} P_A^{1/2}} \tag{6.19}$$

If, $\left(\frac{b_1}{b_2}\right)^{1/2} e^{-\frac{\Delta H_{Ads}}{2RT}} = b'$

Then equation (6.19) will become

$$\theta = \frac{b' P_A^{1/2}}{1 + b' P_A^{1/2}} \tag{6.20}$$

According to above relation, fractional surface coverage is the function of pressure of gas A as given below

$$\theta = f(P_A)$$

Special Cases

(i) When P_A is low, then $1 + b P_A^{1/2} \approx 1$

So, equation (6.20) becomes

$$\theta = b'P_A^{1/2}$$

$$\theta \propto P_A^{1/2}$$

It means θ is directly proportional to $P_A^{1/2}$ (Fig. 6.10).

(ii) When P_A is high, then $1 + bP_A^{1/2} \approx P_A^{1/2}$. So, equation (6.20) becomes

$$\theta = 1$$

It means θ is independent of pressure when P_A is high (Fig. 6.10).

By taking inverse of equation (6.20)

$$\frac{1}{\theta} = \frac{1 + b'P_A^{1/2}}{b'P_A^{1/2}}$$

$$\frac{1}{\theta} = \frac{1}{b'P_A^{1/2}} + 1$$

According to above equation 1/θ is a linear function of $1/P_A^{1/2}$ whose slope equal to 1/b', and intercept equal to 1 as shown in Fig. 6.11.

On comparison of equations (6.11) and (6.20) of non-dissociative and dissociative adsorption respectively, it is concluded that θ is more dependent on pressure for non dissociative adsorption but θ is less dependent on pressure for dissociative adsorption as shown in Fig. 6.12.

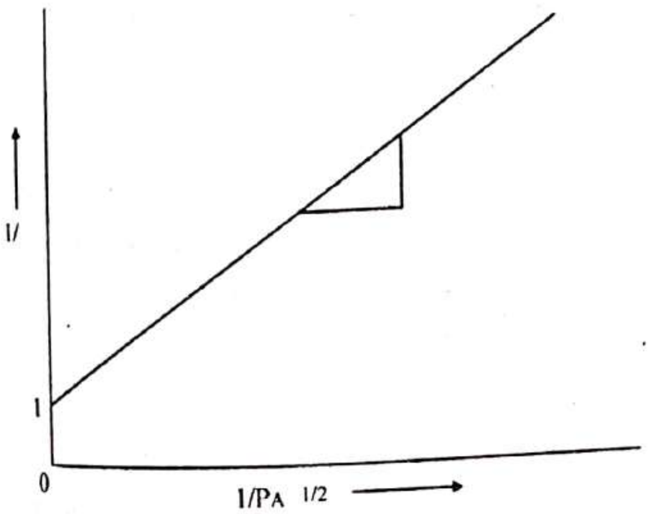


Fig. 6.11 Plot of 1/θ versus $1/P_A^{1/2}$ with intercept 1

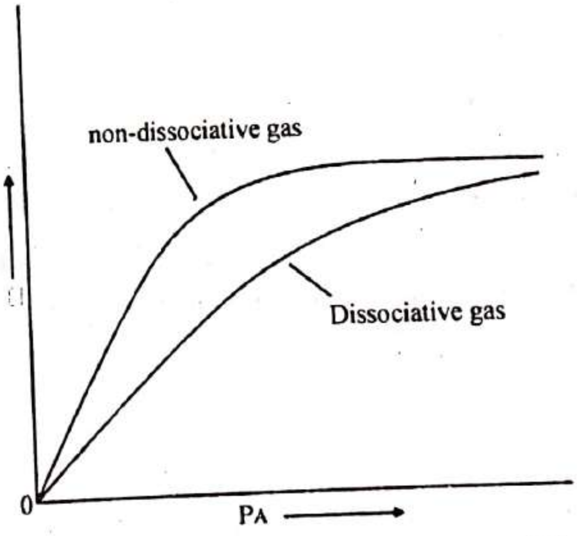


Fig. 6.12 Plot showing dependence of θ on P_A for dissociative and non-dissociative adsorption

Limitations

The Langmuir adsorption isotherm gives a quantitative explanation of the adsorption. The mechanism of chemical adsorption can also be explained with the help of Langmuir equation. The Langmuir adsorption isotherm gives a satisfactory theoretical explanation of a large number of experimental results. But it also has some limitations as Langmuir adsorption isotherm assumes that surface is capable of adsorbing one molecule thick layer. But in actual practice, there are chances of multilayer formation. According to this theory, the saturation value of adsorption should be independent of temperature. But experiments show that saturation value decreases with the rise of temperature. This theory holds good only at low pressure.

Example 6.1

Adsorption of ozone on solid surface takes place according to following scheme

$$O_{3(gas)} \rightleftarrows O_{Ads} + O_{2(Ads)}$$

Write down Langmuir adsorption isotherm for the adsorption.

Solution

According to the reaction given above, ozone is dissociated into two species, therefore Langmuir isotherm for the adsorption of ozone will be

$$\theta = \frac{b'P_{O_3}^{1/2}}{1 + b'P_{O_3}^{1/2}}$$

Example 6.2

Adsorption of ozone on solid surface takes place according to following scheme

$$O_{3(gas)} \rightleftarrows 3O_{(Ads)}$$

Write down Langmuir isotherm for the adsorption of ozone.

Solution

Ozone is dissociated into three oxygen atoms as given in above equation, therefore Langmuir adsorption isotherm is

$$\theta = \frac{b''P_{O_3}^{1/3}}{1 + b''P_{O_3}^{1/3}}$$

Comments: If a gas dissociates into greater number of atoms, then dependence of θ on pressure of gas decreases.

6.6 APPLICATION OF LANGMUIR ADSORPTION ISOTHERM FOR SINGLE SYSTEM

The Langmuir adsorption isotherm for single system can be used for the determination of isosteric enthalpy of adsorption (ΔH_θ) and for the study of catalytic reaction of gas on solid surface.

6.6.1 Determination of Isosteric Enthalpy of Adsorption (ΔH_0)

The variation of pressure of a gas with temperature for a particular fractional surface coverage can be used to determine the enthalpy of adsorption called isosteric enthalpy of adsorption which is represented by ΔH_0.

We know that,

$$\theta = \frac{bP_A}{1+bP_A}$$

$$\theta(1+bP_A) = bP_A$$

$$\theta + (bP_A)\theta = bP_A$$

$$\theta = bP_A(1-\theta)$$

$$bP_A = \frac{\theta}{(1-\theta)}$$

By taking natural logarithm on both sides of above equation

$$\ln(bP_A) = \ln\left(\frac{\theta}{1-\theta}\right) \tag{6.21}$$

As b = k_{Ads}/k_{Des}, so b depends upon temperature because k_{Ads} and k_{Des} are dependent on temperature. Then, relation (6.21) will be

$$\ln P_A + \ln b = \ln\left(\frac{\theta}{1-\theta}\right)$$

By differentiating above equation with respect to T at constant θ, we get

$$\left(\frac{\partial \ln P_A}{\partial T}\right)_\theta + \left(\frac{\partial \ln b}{\partial T}\right)_\theta = \frac{\partial}{\partial T}\left(\ln\frac{\theta}{1-\theta}\right)_\theta \tag{6.22}$$

As θ is constant so, $\frac{\partial}{\partial T}\left(\ln\frac{\theta}{1-\theta}\right)_\theta = 0$. Then equation (6.22) will be,

$$\left(\frac{\partial \ln P_A}{\partial T}\right)_\theta + \left(\frac{\partial \ln b}{\partial T}\right)_\theta = 0$$

$$\left(\frac{\partial \ln P_A}{\partial T}\right)_\theta = -\left(\frac{\partial \ln b}{\partial T}\right)_\theta \tag{6.23}$$

As we know that,

$$\Delta F = -RT\ln K \tag{6.24}$$

According to thermodynamics; $\Delta F = \Delta H_\theta - T\Delta S$. So, equation (6.24) will be

$$\Delta H_\theta - T\Delta S = -RT\ln b$$

$$\ln b = -\frac{\Delta H_\theta}{RT} + \frac{T\Delta S}{RT}$$

$$\ln b = -\frac{\Delta H_\theta}{RT} + \frac{\Delta S}{R}$$

Differentiating the above equation with respect to T, we get

$$\left(\frac{\partial \ln b}{\partial T}\right) = -\frac{\Delta H_\theta}{R}\frac{\partial}{\partial T}\left(T^{-1}\right) + 0$$

$$\left(\frac{\partial \ln b}{\partial T}\right) = +\frac{\Delta H_\theta}{RT^2} \qquad (6.25)$$

Relation (6.25) is called Vant's Hoff equation. By putting the value of $\left(\frac{\partial \ln b}{\partial T}\right)$ from equation (6.25) in equation (6.23), we get

$$\left(\frac{\partial \ln P_A}{\partial T}\right)_\theta = -\frac{\Delta H_\theta}{RT^2}$$

$$\partial \ln P_A = -\frac{\Delta H_\theta}{R}\frac{\partial T}{T^2} \qquad (6.26)$$

Integrating equation (6.26), we get

$$\int \partial \ln P_A = -\frac{\Delta H_\theta}{R}.\int\frac{\partial T}{T^2}$$

$$\ln P_A = +\frac{\Delta H_\theta}{R}\frac{1}{T} + c \qquad (6.27)$$

Where, c is the constant of integration. So, equation (6.27) is an equation of straight line in intercept form. The value of isosteric enthalpy of adsorption can be determined from the slope of the plot of ln P_A as a function of 1/T at constant θ as shown in Fig. 6.13.

The value and sign of ΔH_θ depends upon the nature of interaction between adsorbate and adsorbent. For negative value of enthalpy of adsorption, variation of lnP_A with 1/T is shown in Fig. 6.14.

The value of ΔH_θ is an approximation. Langmuir isotherm does not give an exact value of ΔH_θ because all sites of adsorbent are not equal, so ΔH_θ for every site is different. Moreover occupied sites show hindrance for molecules of adsorbate to fill the vacant sites of adsorbent.

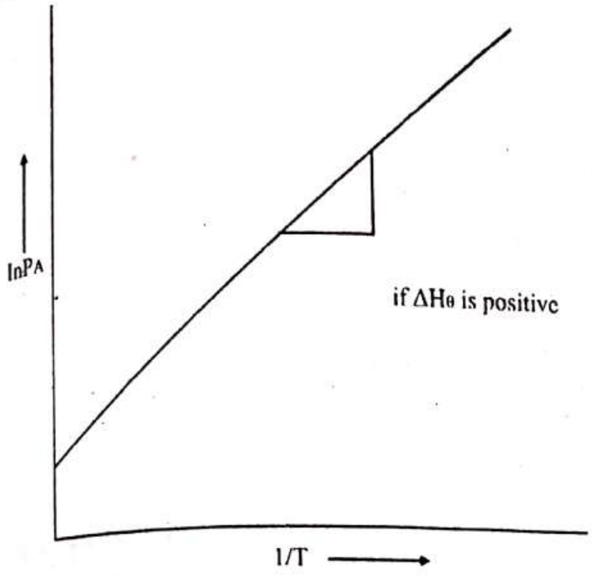


Fig. 6.13 Plot of ln P_A versus 1/T when isosteric enthalpy has positive value

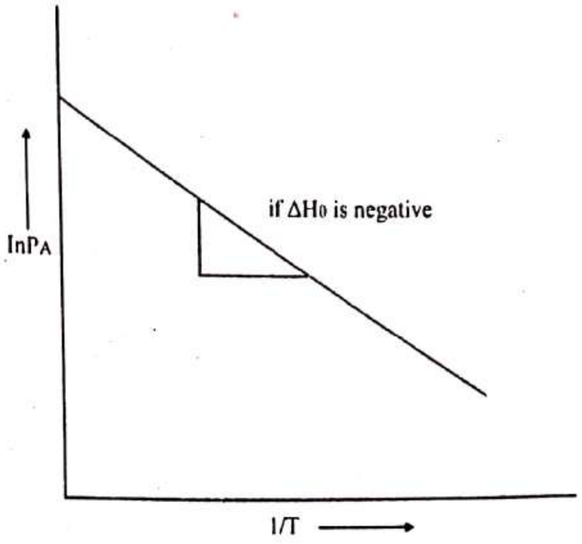


Fig. 6.14 Plot of ln P_A versus 1/T when isosteric enthalpy has negative value

Example 6.3

The pressure required to saturate a particular surface was measured at two different temperatures as given below

P_1= 250 Pa at 25 °C, P_2= 350Pa at 50 °C.

Calculate the isosteric enthalpy of adsorption.

Solution

At pressure P_1 and temperature T_1 equation (6.27) will be

$$\ln P_1 = \frac{\Delta H_\theta}{R}\frac{1}{T_1} + c \qquad (6.27a)$$

At temperature T_2 pressure is P_2 then, equation (6.27) will be

$$\ln P_2 = +\frac{\Delta H_\theta}{R}\frac{1}{T_2} + c \qquad (6.27b)$$

Subtracting equation (6.27a) from equation (6.27b), we get

$$\ln\frac{P_2}{P_1} = \frac{\Delta H_\theta}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\ln\frac{P_1}{P_2} = \frac{\Delta H_\theta}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\ln\frac{P_1}{P_2} = \frac{\Delta H_\theta}{R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$$

$$\Delta H_\theta = R\left(\frac{T_1T_2}{T_2 - T_1}\right)\left(\ln\frac{P_1}{P_2}\right)$$

By putting values in above equation from given data we can find the isosteric enthalpy of adsorption as

$$\Delta H_\theta = 8.3143\left[\frac{(298)(323)}{323-298}\right]\left(\ln\frac{250}{350}\right) = -10.77\text{kJmol}^{-1}$$

6.6.2 Catalytic Reaction of Gas Adsorbed on Solid Surface

The most important feature of Langmuir adsorption isotherm is its application to explain the catalytic reaction of a gas on solid surface. Catalytic reaction of gas on metal surface involve following steps

(a) Diffusion of reactants towards catalyst surface.

(b) Adsorption of reactants on solid surface.

(c) Product formation on catalyst surface.

(d) Desorption of product gas.

(e) Diffusion of product gas into the reaction vessel from catalyst surface. This phenomenon is depicted by pictorial diagram as shown in Fig. 6.15.

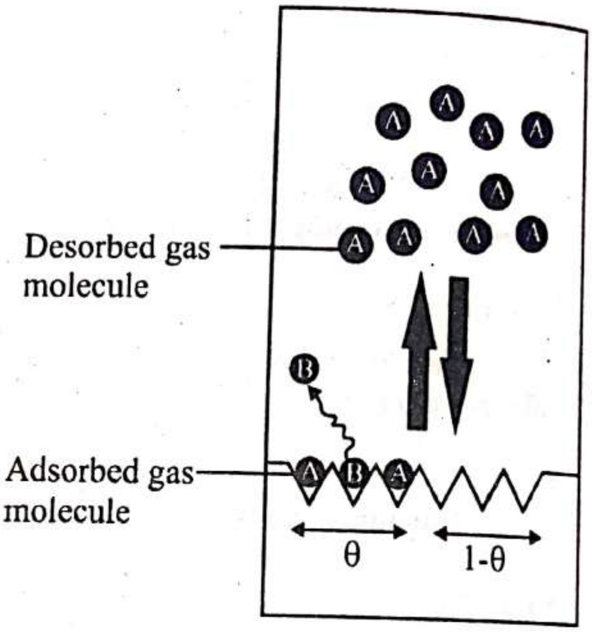


Fig. 6.15 Pictorial diagram of catalytic reaction of two gases on solid surface

According to above steps scheme of catalytic reaction of gas A to generate gas B can be written as

$$A_{(gas)} \underset{\text{diffusion + desorption}}{\overset{\text{diffusion + adsorption}}{\rightleftarrows}} A_{Ads} \qquad \text{(Fast)}$$

$$A_{(Ads)} \xrightarrow[\text{slow}]{k_r} B_{(Ads)}$$

$$B_{(Ads)} \xrightarrow{\text{fast}} B_{(gas)}$$

Where, k_r is the heterogeneous rate constant.

Rate of reaction is directly proportional to fractional surface coverage of adsorbed gas A.

$$\text{Rate of reaction} \propto \theta_A$$

$$\text{Rate} = k_r\theta_A \tag{6.28}$$

According to Langmuir adsorption isotherm for non dissociative adsorption, we know $\theta_A = \frac{bP_A}{1+bP_A}$. So, equation (6.28) will be

$$\text{Rate} = k_r = \frac{bP_A}{1+bP_A} \tag{6.29}$$

Nature of gas, whether it is strongly, moderately or weakly adsorbed on catalyst surface, highly affects kinetics of catalytic reactions. Thus kinetics of catalytic reaction can be discussed in two separate cases as given below

(i) When Reactant Gas is Weakly Adsorbed

If gas is weakly adsorbed it means b is very low. So. $1 + bP_A \approx 1$ put this value in equation (6.29) we get,

$$\text{Rate} = k_r bP_A \tag{6.30}$$

$$\text{Rate} \propto P_A$$

Hence, reaction is of first order, if b is very low.

$$-\frac{dP_A}{dt} = \text{Rate of consumption of gas A}$$

So, equation (6.30) can be written in terms of rate of consumption of gas A

$$-\frac{dP_A}{dt} = k_r bP_A \tag{6.31}$$

By separating variables and integrating equation (6.31) we get,

$$-\int \frac{dP_A}{P_A} = k_r b \int dt \tag{6.32}$$

$$-\ln P_A = k_r bt + c \tag{6.33}$$

Applying boundary conditions, when t = 0 then $P_A = P_i$. Physically, it is said that when reaction just starts then pressure has its maximum value equal to initial pressure of gas.

So, $-\ln P_i = c$, by putting value of c in equation (6.33) we get,

$$-\ln P_A = k_r bt - \ln P_i$$

$$-\ln P_A + \ln P_i = k_r bt$$

$$\ln \frac{P_i}{P_A} = k_r bt \tag{6.34}$$

Results concluded from equation (6.34) are as follows

(i) Equation (6.34) is straight line equation passing through origin.

(ii) Plot of ln P_i/P_A versus t as shown in Fig. 6.16.

(iii) The value of k_r can be determined from slope i.e.

$$\text{Slope} = k_r b$$

$$k_r = \frac{\text{slope}}{b}$$

(iv) Expression of half life of gas A can be derived as

$$t = t_{1/2} \text{ at } P_A = P_i/2$$

Applying this condition to equation (6.34), we get

$$\ln \frac{P_i}{P_i/2} = k_r b t_{1/2}$$

$$k_r b t_{1/2} = \ln 2$$

$$t_{1/2} = \frac{1}{k_r b} \ln 2$$

$$t_{1/2} = \frac{0.693}{k_r b} \quad (6.35)$$

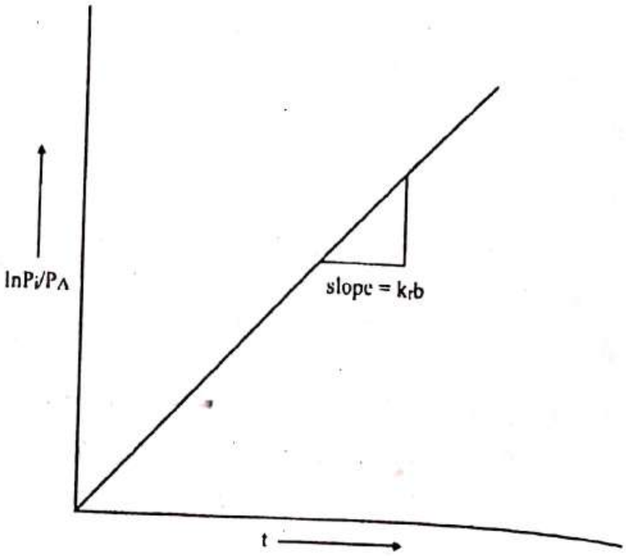


Fig. 6.16 ln P_i/P_A as a function of time

Results can be drawn from equation (6.35) as follows: $t_{1/2}$ is function of b, $t_{1/2}$ is inversely proportional to b and it is independent of P_A. With change in temperature, k_r and b changes which in turn causes a change in $t_{1/2}$.

(v) Units of k_r can be determined as

$$k_r = \frac{1}{bt} \ln \frac{P_i}{P_A}$$

$$k_r = \text{Pa/s}$$

(vi) The pressure of gas as a function of time can be expressed as

$$\frac{P_i}{P_A} = e^{k_r bt}$$

$$\frac{P_A}{P_i} = e^{-k_r bt}$$

$$P_A = P_i e^{-k_r bt} \quad (6.36)$$

According to equation (6.36), value of P_A decreases with increase of time exponentially as shown in Fig. 6.17.

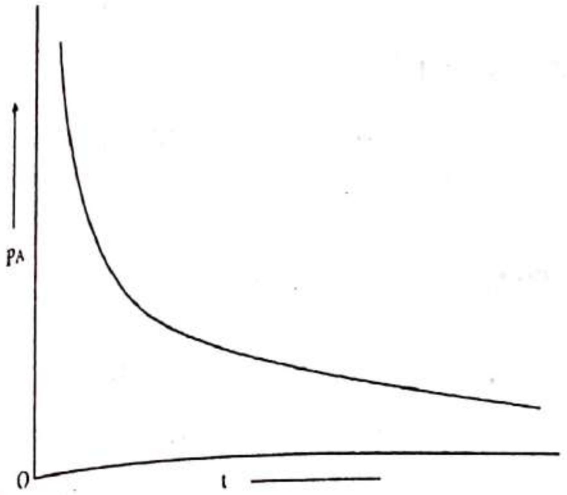


Fig. 6.17 Plot of pressure of gas A versus t in exponential form

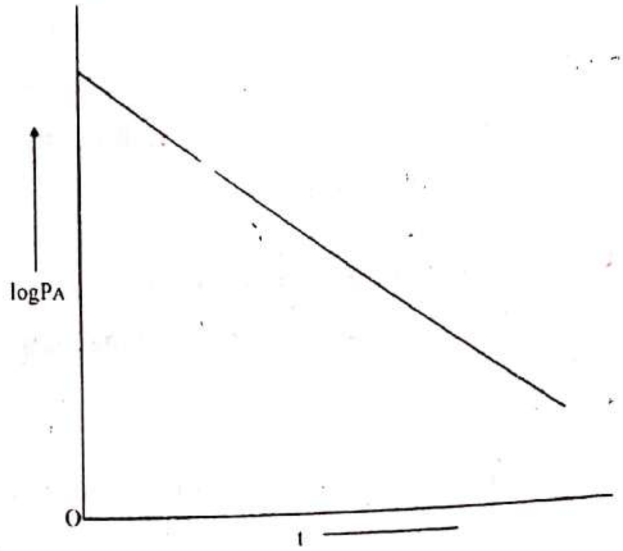


Fig. 6.18 Plot of log P_A versus t

(vii) By converting natural logarithm into common log of equation (6.34), we get

$$2.303 \log \frac{P_i}{P_A} = k_r bt$$

$$\log \frac{P_i}{P_A} = \frac{k_r bt}{2.303}$$

$$\log P_i - \log P_A = \left(\frac{k_r b}{2.303}\right)t$$

$$\log P_A - \log P_i = \left(-\frac{k_r b}{2.303}\right)t$$

$$\log P_A = \log P_i - \left(\frac{k_r b}{2.303}\right)t$$

This is an equation of straight line with intercept and having negative slope as shown in Fig. 6.18. The slope of the plot can be used to determine the value of k_r and intercept can be used to determine the value of initial pressure.

Relation between Homogenous and Heterogeneous Rate Constants

The kinetic rate equation for homogeneous 1st order reaction is

$$\ln \frac{P_i}{P_A} = kt \qquad (6.37)$$

This is the rate law or kinetic rate equation for homogeneous 1st order reaction.

The kinetic rate equation for heterogeneous 1st order reaction is

$$\ln \frac{P_1}{P_A} = k_r bt \tag{6.38}$$

By comparing equation (6.37) and (6.38), we get

$$k = k_r b \tag{6.39}$$

Relation between $(E_a)_{w.a}$ and E_r

According to Arrhenius equation, we know

$$k = Ae^{\frac{E_a}{RT}} \tag{6.40}$$

Taking natural log of above equation,

$$\ln k = -\frac{E_a}{R}\left(\frac{1}{T}\right) + \ln(A) \tag{6.41}$$

Differentiating equation (6.41) with respect to 1/T

$$\frac{d \ln k}{d\,{}^{1}\!/_{T}} \ln k = -\frac{E_a}{R}\frac{d}{d\,{}^{1}\!/_{T}}\left(\frac{1}{T}\right) + 0$$

$$\frac{d \ln k}{d\,{}^{1}\!/_{T}} = -\frac{E_a}{R}$$

$$E_a = -R\frac{d \ln k}{d\,{}^{1}\!/_{T}} \tag{6.42}$$

As $k = k_r b$ and if we put this value of k in equation (6.42), then E_a become $(E_a)_{w.a}$

$$(E_a)_{w.a} = -R\frac{d(\ln k_r b)}{d\,{}^{1}\!/_{T}}$$

$$(E_a)_{w.a} = -R\frac{d}{d\,{}^{1}\!/_{T}}(\ln k_r b)$$

$$(E_a)_{w.a} = -R\frac{d}{d\,{}^{1}\!/_{T}}(\ln k_r + \ln b) \tag{6.43}$$

According to Arrhenius equation, $k_r = A_r e^{-{}^{E_r}\!/_{RT}}$

$$\text{So, } (E_a)_{w.a} = -R\frac{d}{d\,{}^{1}\!/_{T}}\left(\ln A_r e^{\frac{E_r}{RT}} + \ln\left(\frac{b_1}{b_2}\right)e^{\frac{\Delta H_{a,b}}{RT}}\right)$$

$$(E_a)_{w.a} = -R\frac{d}{d\,{}^1\!/_T}\left\{\ln A_r - \frac{E_r}{RT} + \ln\left(\frac{b_1}{b_2}\right) - \frac{\Delta H_{Ads}}{RT}\right\}$$

$$(E_a)_{w.a} = -R\left\{\frac{d}{d\,{}^1\!/_T}\ln A_r - \frac{E_r}{R}\left(\frac{d}{d\frac{1}{T}}\cdot\frac{1}{T}\right) + \frac{d}{d\,{}^1\!/_T}\ln\frac{b_1}{b_2} - \frac{\Delta H_{Ads}}{R}\frac{d}{d\frac{1}{T}}\cdot\frac{1}{T}\right\}$$

$$(E_a)_{w.a} = -R\left\{0 - \frac{E_r}{R} + 0 - \frac{\Delta H_{Ads}}{R}\right\}$$

$$(E_a)_{w.a} = R\left\{\frac{E_r + \Delta H_{Ads}}{R}\right\}$$

$$(E_a)_{w.a} = E_r + \Delta H_{Ads} \qquad (6.44)$$

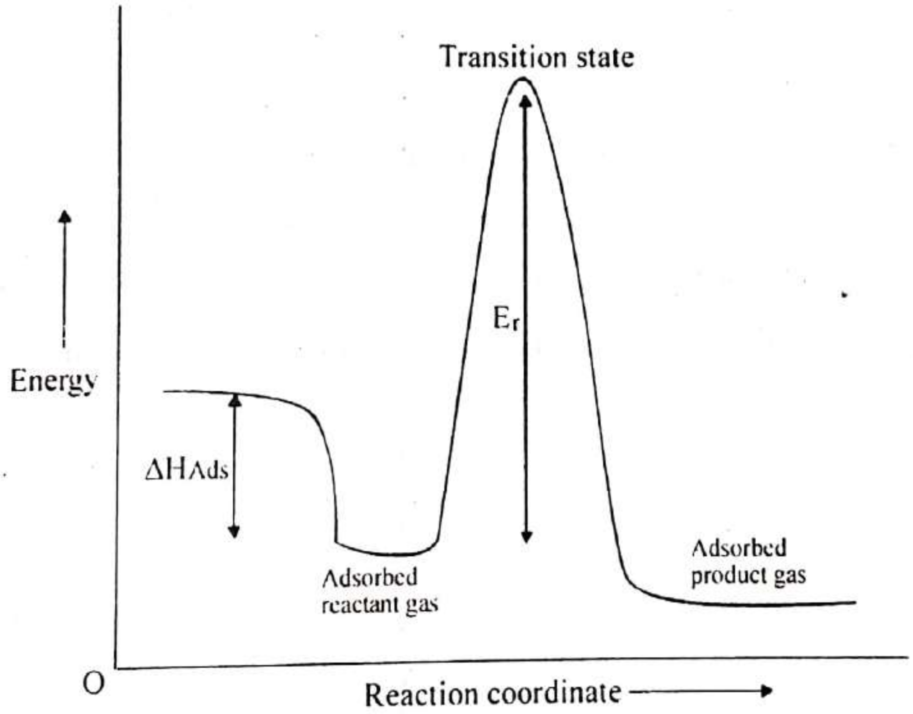


Fig. 6.19 Energy profile showing relative energy of weakly adsorbed gas

(ii) When Gas is Strongly Adsorbed

If gas is strongly adsorbed it means that b is very large so,

$$1 + bP_A \approx bP_A \qquad (6.45)$$

As we know,

$$\text{Rate} = k_r\frac{bP_A}{1 + bP_A} \qquad (6.46)$$

Applying approximation to equation (6.46) from equation (6.45), we get

$$\text{Rate} = k_r \qquad (6.47)$$

It means that order of reaction is zero.

Rate can be expressed in terms of rate of decrease in pressure of gas A as

$$-\frac{dP_A}{dt} = k_r \qquad (6.48)$$

Equation (6.48) is differential equation which can be showed by separating variables as

$$-\int dP_A = k_r \cdot \int dt$$

$$-P_A = k_r t + c \qquad (6.49)$$

Applying boundary conditions, when $t = 0$ then $P_A = P_i$

Put these values in equation (6.49), we get

$$-P_i = k_r(0) + c$$

$$c = -P_i$$

By putting the value of c in equation 6.49, we get

$$-P_A = k_r t - P_i$$

$$P_i - P_A = k_r t \qquad (6.50)$$

Equation (6.50) is rate equation for heterogeneous reaction when gas is strongly adsorbed.

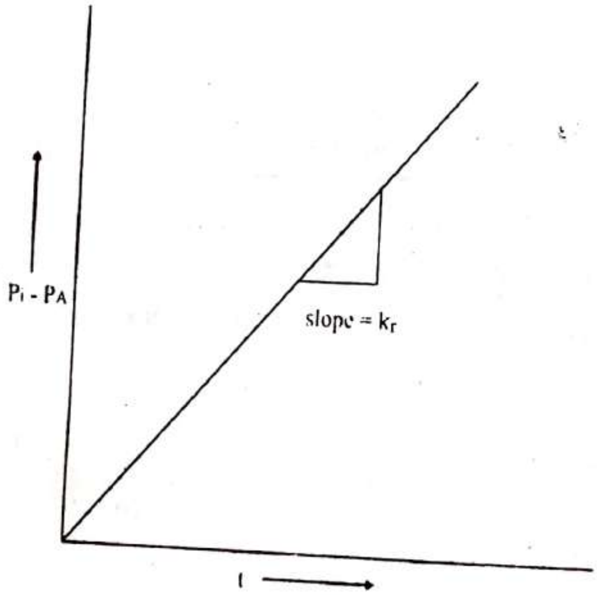


Fig. 6.20 Plot of $P_i - P_A$ as a function of time

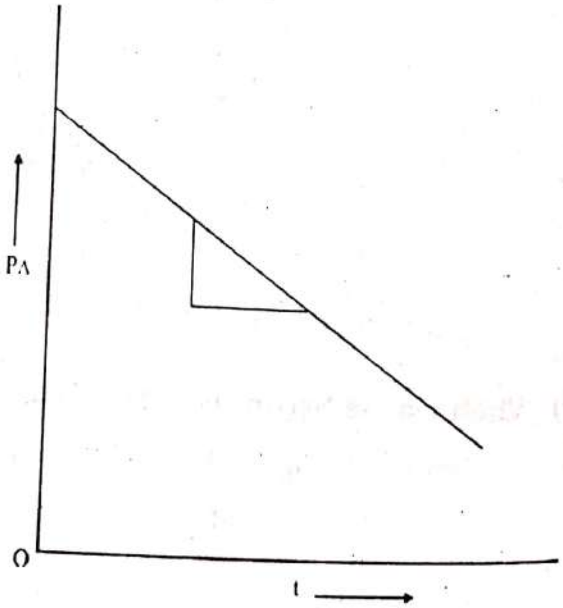


Fig. 6.21 Plot of P_A versus t with intercept and negative slope value

Results concluded from equation (6.50) are as follows

(i) Equation 6.50 is straight line equation passing through origin.

(ii) Plot of ln $(P_i - P_A)$ versus t as shown in Fig. 6.20.

(iii) The value of k_r can be determined from the slope of the plot as shown in Fig. 6.20.

$$\text{slope} = k_r$$

(iv) The half life period of gas A can be expressed as:

$$t = t_{1/2} \text{ at } P_A = P_i/2$$

Applying this condition to equation (6.50)

$$P_i - {}^{P_i}\!/_2 = k_r t_{1/2}$$

$$\frac{P_i}{2} = k_r t_{1/2}$$

$$t_{1/2} = \frac{P_i}{2k_r} \tag{6.51}$$

Results can be drawn from equation (6.51) as follows: $t_{1/2}$ is not a function of b, $t_{1/2}$ is a function of P_i and $t_{1/2}$ is a function of temperature because k_r is a function of temperature.

(v) Rearranging equation (6.50), we get

$$P_A - P_i = -k_r t$$

$$P_A = P_i - k_r t \tag{6.52}$$

Equation (6.52) is an equation of straight line in intercept form with slope equal to $-k_r$ and intercept equal to P_i as shown in Fig. 6.21.

Relation between Homogenous and Heterogeneous Rate Constants

The kinetic rate equation for homogeneous zero order reaction is given as

$$P_i - P_A = kt \tag{6.53}$$

The kinetic rate equation for heterogeneous zero order reaction is

$$P_i - P_A = k_r t \tag{6.54}$$

By comparing equations (6.53) and (6.54) we get,

$$k = k_r \tag{6.55}$$

Relation between $(E_a)_{s.a}$ and E_r

According to Arrhenius equation,

$$k = Ae^{-E_a/RT}$$

Taking natural logarithm of above equation,

$$\ln k = -\frac{E_a}{R}\left(\frac{1}{T}\right) + \ln(A)$$

Differentiating above equation with respect to 1/T

$$\frac{d\ln k}{d\,{}^1\!/_T} = -\frac{E_a}{R}\frac{d}{d\,{}^1\!/_T}\left(\frac{1}{T}\right) + 0$$

$$\frac{d\ln k}{d\,{}^1\!/_T} = -\frac{E_a}{R}$$

$$E_a = -R\frac{d}{d\,{}^1\!/_T}(\ln k) \qquad (6.56)$$

As $k = k_r$ and if we put this value of k in equation (6.56), then E_a become $(E_a)_{s.a}$

$$(E_a)_{s.a} = -R\frac{d}{d\,{}^1\!/_T}(\ln k_r) \qquad (6.57)$$

According to Arrhenius equation, $k_r = A_r e^{-\frac{E_r}{RT}}$

By putting value of k_r in equation (6.57), we get

$$(E_a)_{s.a} = -R\frac{d}{d\,{}^1\!/_T}\left(\ln A_r e^{-\frac{E_r}{RT}}\right)$$

$$(E_a)_{s.a} = -R\frac{d}{d\,{}^1\!/_T}\left(\ln A_r - \frac{E_r}{RT}\right)$$

$$(E_a)_{s.a} = -R\left\{\frac{d}{d\,{}^1\!/_T}\ln A_r - \frac{E_r}{R}\left(\frac{d}{d\frac{1}{T}}\frac{1}{T}\right)\right\}$$

$$(E_a)_{s.a} = -R\left\{0 - \frac{E_r}{R}\right\}$$

$$(E_a)_{s.a} = -R\left(-\frac{E_r}{R}\right)$$

$$(E_a)_{s.a} = E_r \qquad (6.58)$$

(iii) When Gas is Moderately Adsorbed

When gas is moderately adsorbed the order of reaction will be in between of zero and 1st order of reaction. It can be 0.1, 0.2, 0.3 ...0.9.

6.7 LANGMUIR ADSORPTION ISOTHERM FOR DOUBLE SYSTEM

Some adsorbents have an ability to adsorb more than one gas. Langmuir adsorption isotherm for simultaneous adsorption of two gases on an adsorbent can be derived on the basis of same postulates as given in section 6.5.2. in such system, extent of adsorption of a gas is affected by the presence of another gas. For example we have two gases A and B in a container which are going to be adsorbed on a single adsorbent as shown in Fig. 6.22. At any stage of adsorption,

θ_A = Fractional surface covered by gas A

θ_B = Fractional surface covered by gas B

$(1-\theta_A-\theta_B)$ = Fraction of available sites

Rate of adsorption of gas A is proportional to P_A and $1-\theta_A-\theta_B$

$$R_{Ads} \propto P_A$$

$$R_{Ads} \propto (1-\theta_A-\theta_B)$$

Combining above relations,

$$R_{Ads} \propto P_A(1-\theta_A-\theta_B)$$

$$R_{Ads} = k_1P_A(1-\theta_A-\theta_B) \qquad (6.59)$$

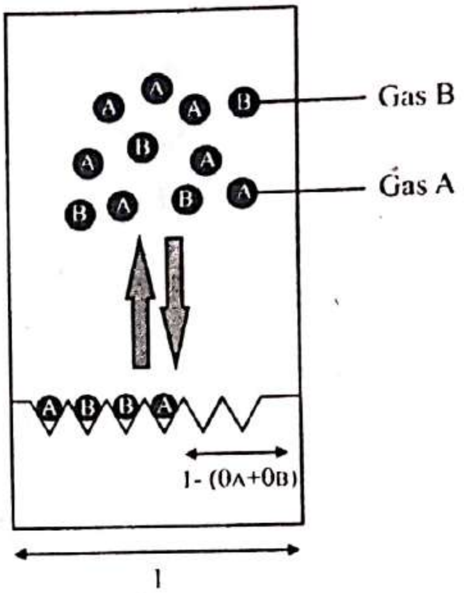


Fig. 6.22 Pictorial diagram of adsorption of two gases on solid surface

R_{Des} of gas A is proportional to fractional surface coverage of gas A.

$$R_{Des} \propto \theta_A$$

$$R_{Des} = k_2\theta_A \qquad (6.60)$$

At equilibrium, rate of adsorption becomes equal to rate of desorption of gas A as given below

$$R_{Ads} = R_{Des}$$

$$k_1P_A(1-\theta_A-\theta_B) = k_2\theta_A \qquad (6.61)$$

The rate of adsorption of gas B is directly proportional to pressure of gas B and fraction of available sites.

$$R_{Ads} \propto P_B$$

$$R_{Ads} \propto (1-\theta_A-\theta_B)$$

Combining above relations,

$$\text{Rate} \propto P_A(1-\theta_A-\theta_B)$$

$$R_{Ads} = k_3P_B(1-\theta_A-\theta_B) \qquad (6.62)$$

The rate of desorption of gas B is proportional to fractional surface coverage of gas B.

$$R_{Des} \propto \theta_B$$

$$R_{Des} = k_4\theta_B \qquad (6.63)$$

At equilibrium,

$$R_{Ads} = R_{Des}$$

$$k_3P_B(1-\theta_A-\theta_B) = k_4\theta_B \qquad (6.64)$$

$$k_4\theta_B = k_3P_B - k_3P_B\theta_A - k_3P_B\theta_B$$

$$k_4\theta_B + k_3P_B\theta_B = k_3P_B - k_3P_B\theta_A$$

$$\theta_B(k_4+k_3P_B) = k_3P_B - k_3P_B\theta_A$$

$$\theta_B = \frac{k_3P_B(1-\theta_A)}{k_4+k_3P_B} \qquad (6.65)$$

By putting value of θ_B from equation (6.65) into equation (6.61), we get

$$k_2\theta_A = k_1P_A\left[1-\theta_A-\frac{k_3P_B(1-\theta_A)}{k_4+k_3P_B}\right]$$

$$k_2\theta_A = k_1P_A\left[\frac{k_4+k_3P_B(1)-(k_4+k_3P_B)\theta_A-k_3P_B(1)+k_3P_B(\theta_A)}{k_4+k_3P_B}\right]$$

$$k_2\theta_A = k_1P_A\left[\frac{k_4+\cancel{k_3P_B}-k_4\theta_A+\cancel{k_3P_B\theta_A}-\cancel{k_3P_B}-\cancel{k_3P_B\theta_A}}{k_4+k_3P_B}\right]$$

$$k_2\theta_A = k_1P_A\left[\frac{k_4-k_4\theta_A}{k_4+k_3P_B}\right]$$

$$k_2\theta_A = k_1P_A\left[\frac{k_4(1-\theta_A)}{k_4+k_3P_B}\right]$$

$$k_2\theta_A(k_4+k_3P_B) = k_1k_4P_A(1-\theta_A)$$

$$k_2\theta_A(k_4+k_3P_B) = k_1k_4P_A - k_1k_4P_A\theta_A$$

$$k_2\theta_A(k_4+k_3P_B) + k_1k_4P_A\theta_A = k_1k_4P_A$$

$$\theta_A \{k_2(k_4 + k_3P_B) + k_1k_4P_A\} = k_1k_4P_A$$

$$\theta_A = \frac{k_1k_4P_A}{k_2(k_4 + k_3P_B) + k_1k_4P_A}$$

$$\theta_A = \frac{k_1k_4P_A}{k_2k_4 + k_2k_3P_B + k_1k_4P_A} \qquad (6.66)$$

Divide numerator and denominator by k_2k_4, we get

$$\theta_A = \frac{\frac{k_1}{k_2}P_A}{1 + \frac{k_3}{k_4}P_B + \frac{k_1}{k_2}P_A} \qquad (6.67)$$

$\frac{k_1}{k_2} = a =$ Adsorption coefficient for gas A

$\frac{k_3}{k_4} = b =$ Adsorption coefficient for gas B

So, equation (6.67) becomes

$$\theta_A = \frac{aP_A}{1 + aP_A + bP_B} \qquad (6.68)$$

By putting value of θ_A in equation (6.65) from equation (6.68), we get

$$\theta_B = \frac{k_3P_B}{k_4 + k_3P_B}\left[1 - \frac{aP_A}{1 + aP_A + bP_B}\right]$$

$$\theta_B = \frac{k_3P_B}{k_4 + k_3P_B}\left[\frac{1 + \cancel{aP_A} + bP_B - \cancel{aP_A}}{1 + aP_A + bP_B}\right]$$

$$\theta_B = \frac{k_3P_B}{k_4 + k_3P_B}\left[\frac{1 + bP_B}{1 + aP_A + bP_B}\right] \qquad (6.69)$$

Divide numerator and denominator of equation (6.69) by k_4

$$\theta_B = \frac{\frac{k_3P_B}{k_4}}{\frac{k_4}{k_4} + \frac{k_3P_B}{k_4}}\left[\frac{1 + bP_B}{1 + aP_A + bP_B}\right]$$

$$\theta_B = \frac{\frac{k_3}{k_4}P_B}{1 + \frac{k_3}{k_4}P_B}\left[\frac{1 + bP_B}{1 + aP_A + bP_B}\right]$$

As we know, $\frac{k_3}{k_4} = b$. So

$$\theta_B = \frac{bP_B}{1+bP_B}\left[\frac{1+bP_B}{1+aP_A+bP_B}\right]$$

$$\theta_B = \frac{bP_B}{1+aP_A+bP_B} \qquad (6.70)$$

Equation (6.68) and (6.70) can be used to find θ_A and θ_B.

According to equation (6.68) and (6.70) adsorption of gas A and B depends upon the adsorption coefficients of gas A and B, and on the pressure of gas A and B.

(i) When both gases are weakly adsorbed then, $1 + bP_B + aP_A \approx 1$. By putting this in equation (6.68)

$$\theta_A = aP_A$$

$$\theta_A \propto P_A$$

By putting above approximation in equation (6.70), we get

$$\theta_B = bP_B$$

$$\theta_B \propto P_B$$

It means that when both gases are weakly adsorbed then adsorption of one gas is not affected by the other.

(ii) When gas A is strongly adsorbed then, $1 + bP_B + aP_A \approx aP_A$. By putting this approximation in equation (6.68), we get

$$\theta_A = \frac{aP_A}{aP_A}$$

$$\theta_A = 1 = \text{Constant}$$

Similarly by putting this approximation in equation (6.70), we get

$$\theta_B = \frac{bP_B}{aP_A}$$

$$\theta_B \propto \frac{P_B}{P_A}$$

So, when gas is strongly adsorbed than the other gas, then all surface which is covered by strongly adsorbed gas which will retard the adsorption of the other gas.

(iii) If both gases are strongly adsorbed then, $1 + bP_B + aP_A \approx aP_A + bP_B$. By putting in equation (6.68)

$$\theta_A = \frac{aP_A}{aP_A + bP_B}$$

By putting above approximation in equation (6.70), we get

$$\theta_B \simeq \frac{bP_B}{aP_A + bP_B}$$

So, when both gases are strongly adsorbed then extent of adsorption of gas is strongly affected by the presence of the other.

6.8 CATALYTIC REACTION OF TWO GASES ON SOLID SURFACE

Generally following steps are involved in catalytic reaction of two gases on solid surface.

(i) Diffusion of reactant towards solid surface

(ii) Adsorption of reactant on solid surface

(iii) Product formation after interaction of reactants

(iv) Desorption of product

(v) Diffusion of product towards gas phase

Catalytic reaction of two gases on a solid surface can take place by one of the following mechanisms: Langmuir Hinshelwood mechanism or Eiley-Rideal mechanism

6.8.1 Langmuir-Hinshelwood Mechanism

Langmuir Hinshelwood mechanism involves the following steps

(i) Diffusion of reactant gases towards solid surface of catalyst.

(ii) Interaction of adsorbed reactant gases on catalyst surface.

(iii) Product formed after interaction of reactants.

(iv) Desorption of product occurs, which is followed by diffusion of product towards gas phase.

Steps of Langmuir Hinshelwood Mechanism in the Form of Chemical Equations

$$A_{(gas)} \overset{R_{(ads)}}{\underset{R_{(des)}}{\rightleftharpoons}} A_{(Ads)}$$

$$B_{(gas)} \rightleftharpoons B_{(Ads)}$$

$$A_{(Ads)} + B_{(Ads)} \xrightarrow{k_r} C_{(Ads)} + D_{(Ads)}$$

$$C_{(Ads)} + D_{(Ads)} \rightleftharpoons C_{(gas)} + D_{(gas)}$$

According to Langmuir Hinshelwood mechanism, the rate of reaction is proportional to fraction of surface covered by A and B i.e.

$$\text{Rate of reaction} \propto \theta_A \qquad (6.71)$$

$$\text{Rate of reaction} \propto \theta_B \tag{6.72}$$

Combining equation (6.71) and (6.72), we get

$$\text{Rate of reaction} = k_r\theta_A\theta_B \tag{6.73}$$

From equation (6.68) and (6.70) by putting values of θ_A and θ_B in equation (6.73)

$$R_{rex} = k_r \frac{(aP_A)(bP_B)}{(1 + aP_A + bP_B)^2}$$

$$R_{rex} = k_r \frac{abP_AP_B}{(1 + aP_A + bP_B)^2} \tag{6.74}$$

Equation (6.74) is the rate expression for the catalytic reaction of two gases on solid following Langmuir-Hinshelwood mechanism.

Depending upon value of adsorption coefficients of gas A and B, following approximations are concluded

(i) When both gases are weakly adsorbed then, $1 + aP_A + bP_B \approx 1$ by putting this approximation in equation (6.74), we get

$$R_{rex} = k_r abP_AP_B$$

$$R_{rex} \propto P_AP_B$$

It is the equation for second order reaction.

(ii) When gas A is strongly adsorbed then, $1 + aP_A + bP_B \approx aP_A$. Putting this approximation in equation (6.74), we get

$$R_{rex} = k_r (ab)\frac{P_AP_B}{(aP_A)^2}$$

$$R_{rex} = k_r \frac{(ab)}{a^2}\frac{P_AP_B}{P_A{}^2}$$

$$R_{rex} = k_r \frac{b}{a}\frac{P_B}{P_A}$$

So, overall order of reaction is zero because order of reaction with respect to A is -1 while order of reaction with respect to B is 1.

The increase in pressure of gas A will decrease the rate of reaction when A is strongly adsorbed. This reduction in rate of reaction is known as "retardation by reactants". Retardation is not only caused by strong adsorption of one reactant gas, high pressure of one of the reactant gases can also cause retardation. For example at constant value of P_B, rate of reaction increases with the increase of P_A upto a certain value. But further increase in pressure of gas A causes reduction in rate of reaction i.e.

If P_B = constant and P_A = variable then

(i) When P_A is very low then, $1 + aP_A + bP_B \approx 1 + bP_B$ equation (6.74) will be

$$R_{rex} = k_r \frac{abP_A P_B}{(1 + bP_B)^2}$$

So, rate of reaction increases with P_A within low range value of P_A

(ii) When P_A is very high then, $1 + aP_A + bP_B \approx aP_A$ the equation (6.74) will be

$$R_{rex} = k_r (ab) \frac{P_A P_B}{(aP_A)^2}$$

$$R_{rex} = k_r \frac{b}{a} \frac{P_B}{P_A} \quad \text{(Retardation by reactants)}$$

So, rate of reaction decreases with high value of P_A.

The value of P_A for which rate of reaction is maximum is called $P_{A(max)}$. After $P_{A(max)}$, retardation by reactant starts as shown in Fig. 6.23.

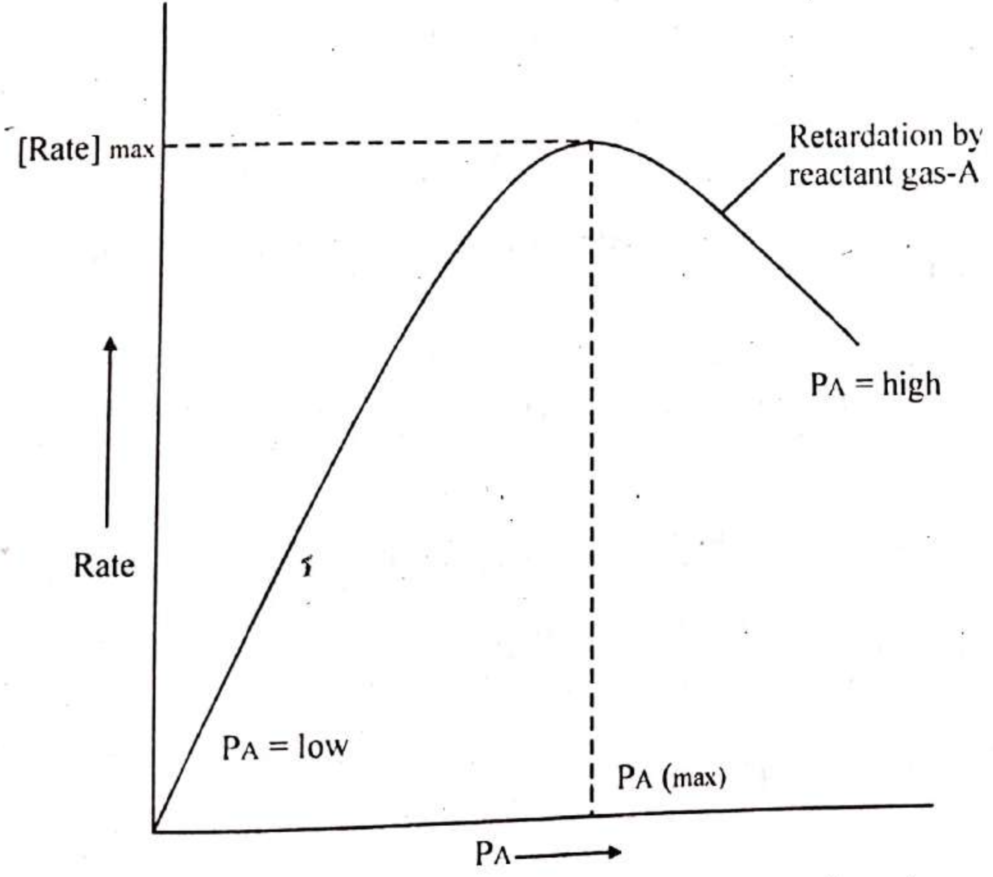


Fig. 6.23 Plot of rate of reaction versus pressure of gas A

Differentiating equation (6.74) with respect to "P_A"

$$\frac{d[\text{Rate}]}{dP_A} = k_r abP_B \frac{d}{dP_A}\left[\frac{P_A}{(1 + aP_A + bP_B)^2}\right]$$

$$\frac{d[\text{Rate}]}{dP_A} = k_r abP_B \frac{d}{dP_A}\left[P_A(1+aP_A+bP_B)^{-2}\right]$$

By applying product rule,

$$\frac{d[\text{Rate}]}{dP_A} = k_r abP_B\left[P_A \cdot \frac{d(1+aP_A+bP_B)^{-2}}{dP_A} + (1+aP_A+bP_B)^{-2}\frac{dP_A}{dP_A}\right]$$

$$\frac{d[\text{Rate}]}{dP_A} = k_r abP_B\left[P_A(-2)(1+aP_A+bP_B)^{-3}\frac{d}{dP_A}(1+aP_A+bP_B)+(1+aP_A+bP_B)^{-2}(1)\right]$$

$$\frac{d[\text{Rate}]}{dP_A} = k_r abP_B\left[\frac{-2P_A}{(1+aP_A+bP_B)^3}\left(\frac{d}{dP_A}(1)+a\frac{dP_A}{dP_A}+b\frac{dP_B}{dP_A}\right)+(1+aP_A+bP_B)^{-2}\right]$$

The derivative of constant is zero. Hence, above equation become,

$$\frac{d[\text{Rate}]}{dP_A} = k_r abP_B\left[\frac{-2aP_A}{(1+aP_A+bP_B)^3}+\frac{1}{(1+aP_A+bP_B)^2}\right]$$

At $[\text{Rate}]_{max}$, the slope of graph is zero and $P_A = P_{A(max)}$

$$0 = k_r abP_B\left[\frac{-2aP_{A(max)}}{(1+aP_{A(max)}+bP_B)^3}+\frac{1}{(1+aP_{A(max)}+bP_B)^2}\right] \qquad (6.75)$$

Equation (6.75) is a product of two quantities which is equal to zero. One quantity on L.H.S must be zero, constant $k_r abP_B$ can't be zero. So,

$$0 = \left[\frac{1}{(1+aP_{A(max)}+bP_B)^2}-\frac{2aP_{A(max)}}{(1+aP_{A(max)}+bP_B)^3}\right]$$

$$\frac{2aP_{A(max)}}{(1+aP_{A(max)}+bP_B)^3} = \frac{1}{(1+aP_{A(max)}+bP_B)^2}$$

$$2aP_{A(max)} = \frac{(1+aP_{A(max)}+bP_B)^3}{(1+aP_{A(max)}+bP_B)^2}$$

$$2aP_{A(max)} = (1+aP_{A(max)}+bP_B)$$

$$2aP_{A(max)} - aP_{A(max)} = 1+bP_B$$

$$aP_{A(max)} = 1+bP_B$$

$$P_{A(max)} = \frac{1+bP_B}{a} \qquad (6.76)$$

Using equation (6.76), we can calculate the value of pressure of gas A at which rate of reaction is maximum. The retardation caused by high pressure of gas A is not much significant, %age decline in rate of reaction from $P_{A(max)}$ to $2P_{A(max)}$ is only 11.1%. It can be proved mathematically as

Rate of Reaction at $P_A = P_{A\,(max)}$

$$[\text{Rate}]_{P_A = P_{A(max)}} = k_r ab\left[\frac{P_{A(max)}P_B}{\left(1 + aP_{A(max)} + bP_B\right)^2}\right] \qquad (6.77)$$

Putting value of $P_{A\,(max)}$ from equation (6.76) into equation (6.77), we get

$$[\text{Rate}]_{P_A = P_{A(max)}} = k_r ab\left[\frac{\left(\frac{1+bP_B}{a}\right)P_B}{\left(1 + a\left(\frac{1+bP_B}{a}\right) + bP_B\right)^2}\right]$$

$$[\text{Rate}]_{P_A = P_{A(max)}} = k_r \frac{ab}{a}\left[\frac{(1+bP_B)P_B}{\left(1 + (1+bP_B) + bP_B\right)^2}\right]$$

$$[\text{Rate}]_{P_A = P_{A(max)}} = k_r b\left[\frac{(1+bP_B)P_B}{\left(2 + 2bP_B\right)^2}\right]$$

$$[\text{Rate}]_{P_A = P_{A(max)}} = \frac{k_r b}{4}\left[\frac{(1+bP_B)P_B}{\left(1 + bP_B\right)^2}\right]$$

$$[\text{Rate}]_{P_A = P_{A(max)}} = \frac{k_r b}{4}\left[\frac{P_B}{\left(1 + bP_B\right)}\right] \qquad (6.78)$$

Rate of Reaction at $P_A = 2P_{A\,(max)}$

$$[\text{Rate}]_{P_A = 2P_{A(max)}} = k_r ab\left[\frac{2P_{A(max)}P_B}{\left(1 + a2P_{A(max)} + bP_B\right)^2}\right] \qquad (6.79)$$

Putting value of $P_{A\,(max)}$ from equation (6.76) into equation (6.79), we get

$$[\text{Rate}]_{P_A = 2P_{A(max)}} = k_r ab\left[\frac{2\left(\frac{1+bP_B}{a}\right)P_B}{\left(1 + 2a\left(\frac{1+bP_B}{a}\right) + bP_B\right)^2}\right]$$

$$[\text{Rate}]_{P_A = 2P_{A(max)}} = 2k_r b\left[\frac{(1+bP_B)P_B}{\left(1 + 2(1+bP_B) + bP_B\right)^2}\right]$$

$$[\mathrm{Rate}]_{P_A=2P_{A(max)}} = 2k_r b\left[\frac{(1+bP_B)P_B}{(1+2+2bP_B+bP_B)^2}\right]$$

$$[\mathrm{Rate}]_{P_A=2P_{A(max)}} = 2k_r b\left[\frac{(1+bP_B)P_B}{(3+3bP_B)^2}\right]$$

$$[\mathrm{Rate}]_{P_A=2P_{A(max)}} = \frac{2}{9}k_r b\frac{(1+bP_B)P_B}{(1+bP_B)^2}$$

$$[\mathrm{Rate}]_{P_A=2P_{A(max)}} = \frac{2k_r b}{9}\frac{P_B}{(1+bP_B)} \tag{6.80}$$

Percentage of rate at $P_A = 2P_{A\,(max)}$

$$\%\text{age Rate} = \frac{[\mathrm{Rate}]_{P_A=2P_{A(max)}}}{[\mathrm{Rate}]_{P_A=P_{A(max)}}}\times 100 \tag{6.81}$$

Substituting values of $[\mathrm{Rate}]_{P_A=2P_{A(max)}}$ and $[\mathrm{Rate}]_{P_A=P_{A(max)}}$

$$\%\text{age Rate} = \frac{\dfrac{2}{9}\dfrac{k_r b(P_B)}{(1+bP_B)}}{\dfrac{k_r b}{4}\left(\dfrac{P_B}{1+bP_B}\right)}\times 100$$

$$\%\text{age Rate} = \frac{\frac{2}{9}}{\frac{1}{4}}\times 100$$

$$\%\text{age Rate} = \frac{2\times 4}{9}\times 100$$

$$\%\text{age Rate} = \frac{8}{9}\times 100$$

$$\%\text{age Rate} = 88.9\%$$

%age decline in rate $= 100 - 88.9 = 11.1\%$ of maximum rate

"The decline in rate is difference or reduction in rate when pressure changes from $P_A = P_{A\,(max)}$ to $P_A = 2P_{A\,(max)}$" as shown in Fig. 6.24.

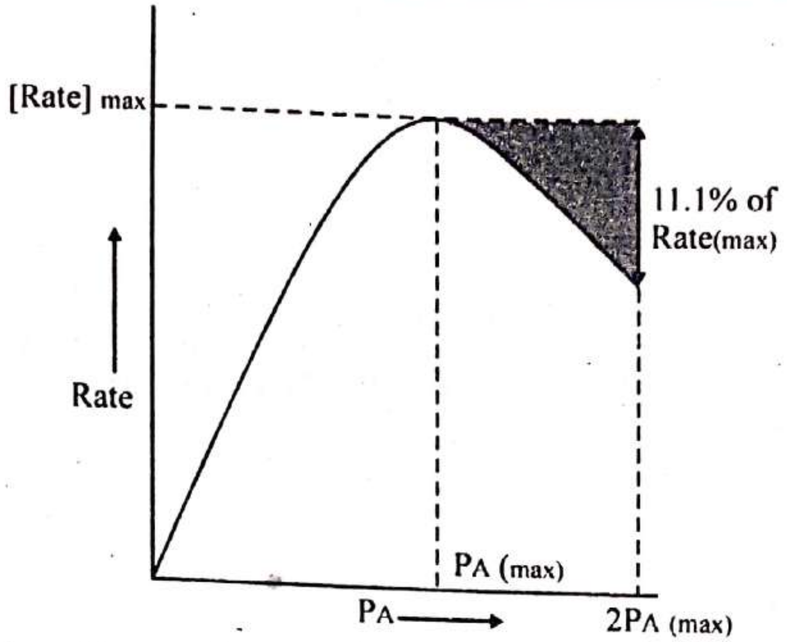


Fig. 6.24 Rate of reaction as a function of P_A showing decline rate at $2P_{A(max)}$

Example 6.4

A catalytic reaction following Langmuir Hinshelwood mechanism was carried out in a container containing solid catalyst at a constant pressure of gas B equal to 200 Pa. The values of adsorption coefficients of gas A and B are 0.2 and 0.35 Pa^{-1} respectively. Calculate the value of P_A, at which the rate of reaction is maximum.

Solution

The value of P_A at which the rate of reaction is maximum i.e. $P_{A(max)}$, can be calculated using equation (6.76), according to which

$$P_{A(max)} = \frac{1 + bP_B}{a}$$

$$P_{A(max)} = \frac{1 + (0.35)(200)}{0.2} = 355Pa$$

6.8.2 Eiley-Rideal Mechanism

Eiley-Rideal mechanism involves the following steps

(i) One reactant get adsorb on surface of catalyst.

(ii) Second reactant doesn't adsorb on catalyst surface. Instead it interact with adsorb reactant. In E-R mechanism, both reactants adsorb on catalyst surface. This is different from Langmuir-Hinshelwood mechanism. In L-H mechanism both reactants adsorb on catalyst surface.

(iii) After interaction products are formed. Later adsorbed product diffuses into reaction vessel after desorption.

However, product can remain in gaseous state and doesn't adsorb on catalyst surface in E-R mechanism.

Scheme of Eiley-Rideal (E-R) Mechanism

Reactant gases A and B are going to be converted into products C and D by following mechanism according to E-R mechanism.

$$A_{(gas)} \rightleftharpoons A_{(Ads)}$$

$$A_{(Ads)} + B_{(gas)} \rightleftharpoons C_{(gas)} + D_{(gas)}$$

According to E-R mechanism, rate of reaction is directly proportional to fraction of the surface covered by gas A and pressure of gas B, because adsorbed molecules of gas A interact with gaseous B to form product i.e.

$$\text{Rate of reaction} \propto \theta_A$$

$$\text{Rate of reaction} \propto P_B$$

Hence,

$$\text{Rate of reaction} = k_r \theta_A P_B \tag{6.82}$$

Rate of reaction is independent of P_A, as θ_A depends upon P_A. For double system, we have

$$\theta_A = \frac{aP_A}{1 + aP_A + bP_B}$$

Then equation (6.82) will be

$$\text{Rate} = k_r \frac{aP_A P_B}{1 + aP_A + bP_B} \tag{6.83}$$

This is a rate law expression for the catalytic reaction of two gases on solid surface following E-R mechanism. Since, B is not an adsorbing specie so, $b \approx 0$ then,

$$1 + aP_A + bP_B \approx 1 + aP_A$$

So, equation (6.83) will be,

$$\text{Rate} = k_r \frac{aP_A P_B}{1 + aP_A}$$

$$\text{Rate} = k_r \left(\frac{aP_A}{1 + aP_A}\right) P_B \tag{6.84}$$

Terms in bracket is related to gas A, it has factor aP_A which can increase or decrease rate of reaction. We reach at following results

(i) When the partial pressure of gas A is very low then, $1 + aP_A \approx 1$. So, equation (6.84) will be,

$$\text{Rate} = k_r a P_A P_B$$

If partial pressure of gas A is low, then reaction will be 2nd order reaction.

(ii) When pressure of gas A is very high then, $1+aP_A \approx aP_A$. So, equation (6.84) will be,

$$\text{Rate} = k_r \frac{aP_AP_B}{aP_A}$$

$$\text{Rate} = k_rP_B$$

Above equation shows, when P_A is very high, then reaction will be 1st order. It also shows that, when P_A is very high then rate of reaction is independent of extent of adsorption of gas A.

6.9 CATALYTIC INORGANIC REACTIONS

6.9.1 Catalytic Oxidation of Carbon Monoxide (CO)

Carbon monoxide can be converted into carbon dioxide by heterogeneous catalysis i.e.

$$CO_{(gas)} + O_{2(gas)} \xrightarrow{Pt_{(s)}} CO_{2(gas)}$$

Important features of reaction are as follows

It is a heterogenous catalytic reaction because catalyst is in solid form and reactants are in gaseous phase. It is a simple reaction and can be considered as an example of double system. In this case both reactants are diatomic molecules. One reactant is a homonuclear i.e. O_2 having non polar nature while, CO is heteronuclear as having two different atoms having slightly polar nature. CO is strongly adsorbed on platinum surface because it is π acceptor ligand and has polar nature. O_2 is weakly adsorbed as it is non polar and has no π acceptor ligand ability. So, it can't easily form strong bond with catalyst, e.g. Pt, Pd etc.

The experimental rate law computed by earlier studies is

$$\text{Rate} \propto \frac{P_{O_2}}{P_{CO}}$$

According to Langmuir Hinshelwood mechanism, the reaction scheme can be written as

$$CO_{(gas)} \rightleftharpoons CO_{(Ads)}$$

$$O_{2(gas)} \rightleftharpoons O_{2(Ads)}$$

$$O_{2(Ads)} + CO_{(Ads)} \xrightarrow{k_r} CO_{2(Ads)}$$

$$CO_{2(Ads)} \rightleftharpoons CO_{2(Des)}$$

$$R_{rex} \propto \theta_{O_2} \qquad (6.85)$$

$$R_{rex} \propto \theta_{CO} \qquad (6.86)$$

By combining equations (6.85) and (6.86)

$$R_{rex} \propto \theta_{O_2}\theta_{CO}$$

$$R_{rex} = k_r\theta_{O_2}\theta_{CO} \tag{6.87}$$

Putting values of θ_{O_2} and θ_{CO} in equation (6.87),

$$R_{rex} = k_r\frac{(aP_{O_2})(bP_{CO})}{(1+aP_{O_2}+bP_{CO})^2} \tag{6.88}$$

As CO is strongly adsorbed, so b >>>> a. Then $1+aP_{O_2}+bP_{CO} \approx bP_{CO}$. By putting this approximation in equation (6.88), we get

$$R_{rex} = k_r\frac{abP_{O_2}P_{CO}}{(bP_{CO})^2}$$

$$R_{rex} = k_r\frac{a}{b}\left(\frac{P_{O_2}}{P_{CO}}\right)$$

As k_r and a/b are constants. So,

$$\text{Rate} \propto \frac{P_{O_2}}{P_{CO}}$$

Hence rate of formation of CO_2 is first order with respect to P_{O_2} and negative first order with respect to P_{CO}. So it is a zero order reaction.

6.9.2 Catalytic Decomposition of Ammonia (NH_3)

Ammonia is commercially produced by Haber's process which is a catalytic process. Its synthesis reaction is reversible. Nitrogen gas (N_2) and hydrogen gas (H_2) are produced o decomposition of ammonia.

$$2NH_{3(gas)} \xleftrightarrow{\text{Catalyst}} N_{2(gas)} + 3H_{2(gas)}$$

Important features of reaction are as follows

It is a catalytic reaction which is an example of heterogeneous catalysis because catalyst is in solid state and reactant is in gaseous state. Catalyst used in this reaction may be Pt, Pd, and Fe. But Pt and Pd are expensive, so Fe is used on industrial scale. It is a reversible process, so catalyst increases rate of formation as well as rate of decomposition of NH_3.

It is experimentally proved that the rate of decomposition of ammonia is directly related to pressure of ammonia and inversely proportional to pressure of hydrogen by the expression give below.

$$\text{Rate of decomposition of } NH_3 \propto \frac{P^m_{NH_3}}{P^n_{H_2}} \tag{6.89}$$

One of the suggested mechanisms for catalytic decomposition of NH_3 on the iron (Fe) surface is stepwise removal of hydrogen atom from NH_3 molecule. The scheme of the reaction is given below.

$$NH_{3(gas)} \overset{Fe}{\rightleftharpoons} NH_{3(Ads)}$$

$$NH_{3(gas)} \rightleftharpoons NH_{2(Ads)} + H_{(Ads)}$$

$$NH_{2(Ads)} \rightleftharpoons NH_{(Ads)} + H_{(Ads)}$$

$$NH_{(Ads)} \rightleftharpoons N_{(Ads)} + H_{(Ads)}$$

$$2N_{(Ads)} \xrightarrow{slow} N_{2(gas)} \qquad \text{(Rate determining step)}$$

$$2H_{(Ads)} \overset{fast}{\rightleftharpoons} H_{2(gas)}$$

Desorption of nitrogen is rate determining step. So, rate of decomposition of ammonia depends upon this step.

Tempkin Adsorption Isotherm for Decomposition of NH_3

Tempkin gave an adsorption isotherm to explain the adsorption-desorption of nitrogen on iron surface. According to this isotherm, rate of adsorption and desorption are exponentially related to fractional surface coverage.

$$R_{Ads} \propto P_{N_2}$$

$$R_{Ads} \propto \frac{1}{e^{g\theta_N}}$$

Where, "g" is a roughness factor which indicates heterogeneity of surface of adsorbent and related to activation energy of adsorption. θ_N is fractional surface coverage of nitrogen gas.

$$R_{Ads} = k_a \frac{P_{N_2}}{e^{g\theta_N}}$$

$$R_{Ads} = k_a P_{N_2} e^{-g\theta_N} \qquad (6.90)$$

By increasing P_{N2}, R_{Ads} increases. But by increasing θ_N, R_{Ads} decreases exponentially.

Rate of desorption of nitrogen is

$$R_{Des} \propto e^{h\theta_N}$$

$$R_{Des} = k_d e^{h\theta_N} \qquad (6.91)$$

Rate of desorption of nitrogen is exponentially related to fractional surface coverage of nitrogen (θ_N).

At equilibrium stage, rate of adsorption becomes equal to rate of desorption of nitrogen as

$$R_{Ads} = R_{Des}$$

$$k_a P_{N_2} e^{-g\theta_N} = k_d e^{h\theta_N}$$

$$\frac{k_a}{k_d} P_{N_2} = \frac{e^{h\theta_N}}{e^{-g\theta_N}}$$

As, $a = \frac{k_a}{k_d}$ so, above equation becomes

$$aP_{N_2} = e^{h\theta_N} e^{g\theta_N}$$

$$aP_{N_2} = e^{\theta_N(h+g)}$$

Let, $h + g = f$

$$aP_{N_2} = e^{f\theta_N}$$

Taking natural logarithm of above equation

$$\ln\left(aP_{N_2}\right) = \ln\left(e^{f\theta_N}\right)$$

$$\ln\left(aP_{N_2}\right) = f\theta_N$$

$$\theta_N = \frac{\ln\left(aP_{N_2}\right)}{f} \tag{6.92}$$

From equation (6.92) putting the value of θ_N into equation (6.91), we get

$$R_{Des} = k_d e^{h\left(\frac{1}{f}\ln\left(aP_{N_2}\right)\right)}$$

$$R_{Des} = k_d e^{\ln\left(aP_{N_2}\right)\frac{h}{f}}$$

$$R_{Des} = k_d \left(aP_{N_2}\right)^{\frac{h}{f}} \tag{6.93}$$

As, $\left(R_{Des}\right)_{N_2} = \left(R_{Decomposition}\right)_{NH_3}$

Then, equation (6.93) will be,

$$\left(R_{Decomposition}\right)_{NH_3} = k_d \left(aP_{N_2}\right)^{\frac{h}{f}} \tag{6.94}$$

As we know that, $2NH_{3(g)} \rightleftharpoons N_{2(gas)} + 3H_{2(gas)}$

$$K = \frac{P^2_{NH_3}}{P_{N_2} P^3_{H_2}}$$

Where, K is the equilibrium constant.

$$P_{N_2} = \frac{P^2_{NH_3}}{P^3_{H_2} . K} \qquad (6.95)$$

Putting the value of P_{N_2} from equation (6.95) into equation (6.94)

$$\left(R_{Decomposition}\right)_{NH_3} = k_d \left(a \frac{P^2_{NH_3}}{P^3_{H_2} . K} \right)^{\frac{h}{f}}$$

$$\left(R_{Decomposition}\right)_{NH_3} = k_d \left(\frac{a}{K}\right)^{\frac{h}{f}} \left(\frac{P^2_{NH_3}}{P^3_{H_2}}\right)^{\frac{h}{f}} \qquad (6.96)$$

a, h and f are constants. The value of h/f may be 0 to 1.

(i) When value of h/f is equal to 0 then, equation (6.96) will be,

$$\left(R_{Decomposition}\right)_{NH_3} = k_d$$

Hence, the rate of decomposition of ammonia is independent of pressure of NH_3 and H_2.

(ii) When the value of h/f is equal to 1 then equation (6.96) will be,

$$\left(R_{Decomposition}\right)_{NH_3} = k_d \left(\frac{a}{K}\right) \left(\frac{P^2_{NH_3}}{P^3_{H_2}}\right)$$

$$\left(R_{Decomposition}\right)_{NH_3} \propto \left(\frac{P^2_{NH_3}}{P^3_{H_2}}\right)$$

Hence, the rate of decomposition of ammonia is dependent on pressure of NH_3 and H_2 at maximum value of h/f.

6.10 CATALYSIS OR USE OF CATALYST IN INDUSTRY

80% of reactions in world are catalytic reactions. Out of this, more than 90 % reactions in industry are also catalytic reactions.

(1) Fertilizer Industry

The 1st step of urea synthesis in Haber's process is catalytic in which the synthesis of ammonia can be done. The reaction is reversible and catalytic as given below

$$N_{2(gas)} + 3H_{2(gas)} \xrightleftharpoons{Fe} 2NH_{3(gas)}$$

(2) Production of CO_2

Most of the refreshing drinks in world are carbonated. Hence, on large scale CO_2 is required. One of the methods of preparation of CO_2 is the catalytic oxidation of CO given as

$$CO_{(gas)} + O_{2(gas)} \xrightarrow{Pt_{(s)}} CO_{2(gas)}$$

(3) Production of H_2SO_4

H_2SO_4 is widely used in industry and academic institutes. The basic step of H_2SO_4 synthesis involves catalytic oxidation of SO_2 as follows

$$2SO_{2(g)} + O_{2(g)} \underset{}{\overset{V_2O_5}{\rightleftharpoons}} 2SO_{3(g)}$$

(4) Hydrogenation

This heterogenous catalytic process is used to convert oils into vegetable ghee. In this reaction, unsaturated hydrocarbons or their derivatives are converted into saturated hydrocarbons or their derivatives. For example, ethene is converted into ethane by hydrogenation.

$$CH_2 = CH_{2(g)} + H_{2(g)} \xrightarrow{Ni} CH_3 - CH_{3(g)}$$

(5) Production of Hydrogen Gas

Hydrogen gas is prepared on industrial scale by the following heterogeneous catalytic processes as given below

$$CH_3OH \xrightarrow{Al_2O_3} H_2 + CO$$

Methanol

$$HCOOH \xrightarrow{Au/Ag} H_2 + CO_2$$

Formic acid

(6) Cracking in Petroleum Industry

Cracking is the process of breaking long-chain hydrocarbons into lower molecular weight hydrocarbons. The rate of cracking is dependent on the temperature and presence of catalyst. Hence, cracking process in petroleum industry is catalytic in nature.

(7) Petroleum Reforming

Catalytic reforming is the process used to convert the linear chain hydrocarbons into the branched chain hydrocarbons in the presence of catalyst. Petroleum reforming can be done in industry on this basis. Reforming increases the burning capability and thus increases the octane number.

$$n-\text{octane} \xrightarrow{\text{Reforming}} 2,2,3-\text{trimethyl pentane}$$

(8) **Redox Reaction**

$$2CH_3OH \xrightarrow{LiAlH_4} CH_4 + [O]$$

It is a reduction process.

6.10.1 Problems in Use of Catalyst in Industry

(1) Sintering

"The retardation in catalytic activity due to aggregation of particles of same size and decrease in surface area called sintering." Promoters perform two functions: avoid sintering and enhance the activity of catalyst. Promoters occupied the space between particles and resist sintering.

U.S nitration fixation laboratory has done work on promoters. Brunaure and Emmet use Fe_2O_3 and Al_2O_3 together as catalyst. Here, Fe_2O_3 is catalyst and Al_2O_3 is promoter.

One or more than one promoter can be used along with catalyst in reactions. e.g. Fe_2O_3+ Al_2O_3 is a singly promoted catalyst having only one promoter.

Doubly promoted catalyst has 2 promoters e.g. Fe_2O_3 acts as a catalyst while Al_2O_3 and K_2O can act as promoters in combination of Fe_2O_3, Al_2O_3 and K_2O.

(2) Ostwald Ripening

Big particles provide attachment site for small particles, so small particles attach on a big particle and form coagulates. Catalyst in this way loses its activity, because Ostwald ripening results in reduction of surface area.

(3) Catalytic Poisoning

Impurity will cause catalytic poisoning. If adsorbing ability of impurities is greater than the adsorbing ability of reactants, then impurities will adsorb on catalyst and occupy active sites. Reactants do not adsorb and retardation occurs. Catalytic poisoning may be permanent or temporary.

6.11 ADVANCED APPROACH TO HOMOGENEOUS CATALYSIS

"In homogeneous catalysis reactants and catalyst both are in same phase." Some examples of homogeneous catalysis are as follows

(1) Autocatalysis

(2) Enzyme catalysis

(3) Acid or base catalysis

6.11.1 Autocatalysis

"A type of catalysis in which one of the products formed act as a catalyst is called autocatalysis."

The chemical reaction between acidified potassium permanganate ($KMnO_4$) and oxalic acid is an example of autocatalysis. The plot of concentration of product as a function of time is given in the Fig. 6.25. It is clear from the Fig. that the concentration of product increases with time very slowly at initial stages of reaction. After this, rapid increase in concentration of product with time indicates that one of the products act as catalyst which speeds up the reaction. The chemical reaction is

$$5(COOH)_2 \cdot 2H_2O + 2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 10CO_2$$

Where, $MnSO_4$ acts as an autocatalyst.

Kinetics of Autocatalysis

Kinetics of autocatalysis involves following general scheme of reactions.

$$A \longrightarrow B + C \qquad (i)$$

$$A + B \xrightarrow{k_1} B + B + C \qquad (ii)$$

Where, (i) is a simple reaction and (ii) is an autocatalytic reaction. Kinetics of reaction (ii) can be discussed under following two cases

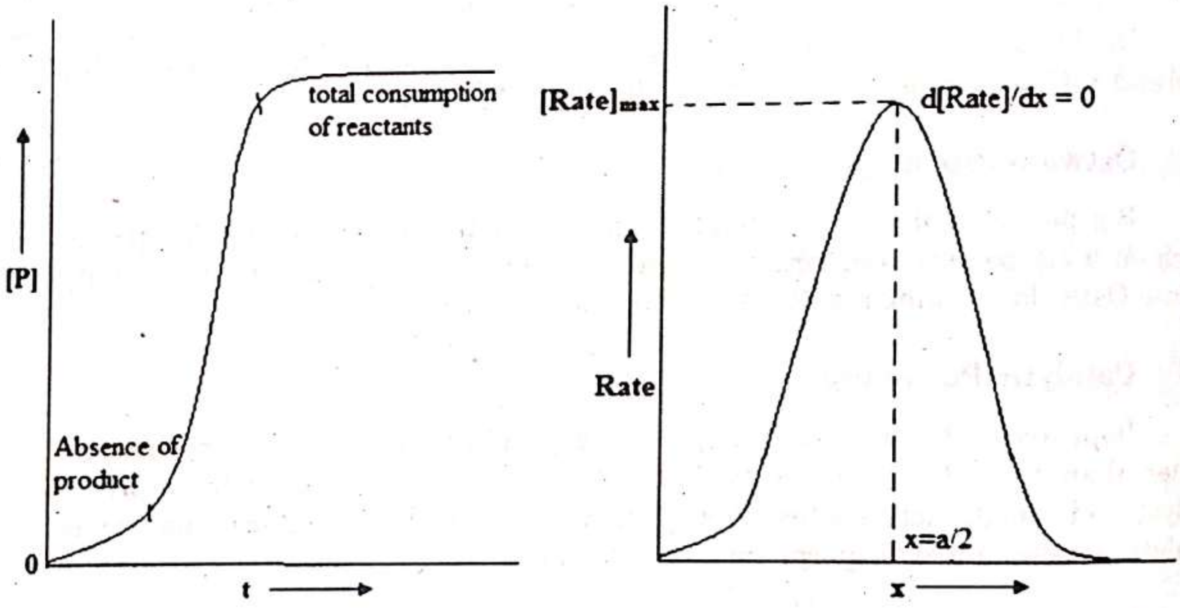


Fig. 6.25 Plot of concentration of product as a function of time for autocatalytic reaction

Fig. 6.26 Plot of rate of reaction versus concentration of autocatalyst

Case 1: When Initial Concentration of Autocatalyst B is Zero

Reaction (ii) is a 2nd order reaction and rate law expression for this reaction is

$$\frac{dx}{dt} \propto [A][B]$$

$$\frac{dx}{dt} \propto (a-x)(x)$$

$$\frac{dx}{dt} = k_1(a-x)(x) \qquad (6.97)$$

Equation (6.97) is the differential form of rate law. Rate of autocatalytic reaction depends upon the concentration of reactant and autocatalyst at time t.

When x = 0, equation (6.97) will be,

$$\frac{dx}{dt} = k_1(a-0)(0) = 0$$

Rate of reaction increases with the increase of x initially and then decreases with increase of x as shown in Fig. 6.26. Using concept of maxima, value of concentration of autocatalyst can be determined at which rate of reaction is maximum. It is depicted from Fig. 6.26 if x is less or greater than a/2 then rate is less than $[\text{rate}]_{\text{max}}$. Rate is maximum, if x = a/2.

From equation (6.97), we have

$$\text{Rate} = k_1(a-x)(x)$$

By differentiating above equation with respect to x, we get

$$\frac{d(\text{Rate})}{dx} = \frac{d}{dx}(k_1ax - k_1x^2)$$

At maxima, $\frac{d(\text{Rate})}{dx}$ will be 0. So,

$$0 = k_1a - 2k_1x$$

$$k_1a = 2k_1x$$

$$x = \frac{a}{2}$$

Case 2: When Initial Concentration of Autocatalyst is not Zero

Rate of reaction is low when reaction is started without catalyst, but rate of reaction can be increased by adding some quantity of catalyst with reactant. Since, catalyst is also generated in autocatalysis therefore concentration of autocatalyst B increases with progress of reaction while, concentration of reactant decreases with reaction progress. If we have a and b as initial concentration of reactant A and autocatalyst B respectively, then

$$A \longrightarrow B + C \qquad \text{(i)}$$

$$A + B \xrightarrow{k_1} B + B + C \qquad \text{(ii)}$$

At t = 0 a b

At time=t a-x b+x

Rate law expression for the reaction (ii) is

$$\frac{dx}{dt} \propto [A][B]$$

$$\frac{dx}{dt} \propto (a-x)(b+x)$$

$$\frac{dx}{dt} = k_1(a-x)(b+x) \tag{6.98}$$

By separating variables and integrating equation (6.98), we get

$$\int \frac{dx}{(a-x)(b+x)} = k_1 \int dt \tag{6.99}$$

Equation (6.99) can be solved by partial fractions as

$$\frac{1}{(a-x)(b+x)} = \frac{A}{a-x} + \frac{B}{b+x} \tag{6.100}$$

$$1 = A(b+x) + B(a-x) \tag{6.101}$$

When b+x = 0 then x = -b, by putting value of x in equation (6.101), we get

$$1 = 0 + B(a+b)$$

$$B = \frac{1}{(a+b)} \tag{6.102}$$

When a-x = 0 then x = a, by putting value of x in equation (6.101), we get

$$1 = A(a+b)$$

$$A = \frac{1}{(a+b)} \tag{6.103}$$

Putting values of A and B from equation (6.103) and (6.102) in equation (6.100), we get

$$\frac{1}{(a-x)(b+x)} = \frac{1}{(a+b)(a-x)} + \frac{1}{(b+x)(a+b)}$$

By putting the value of 1/(a-x)(b+x) in equation (6.99) from above equation we get,

$$\int \frac{dx}{(a-x)(b+x)} = \frac{1}{(a+b)}\left[\int \frac{dx}{(a-x)} + \int \frac{dx}{(b+x)}\right]$$

$$\int \frac{dx}{(a-x)(b+x)} = \frac{1}{(a+b)}\left[-\ln(a-x) + \ln(b+x)\right]$$

$$\int \frac{dx}{(a-x)(b+x)} = \frac{1}{(a+b)} \ln\frac{(b+x)}{(a-x)}$$

Now equation (6.99) becomes,

$$\frac{1}{(a+b)}\ln\frac{(b+x)}{(a-x)} = k_1t + c \qquad (6.104)$$

By applying initial conditions, we can determine the value of integration constant c.

When t = 0, then x = 0

Then equation (6.104) will be,

$$\frac{1}{(a+b)}\ln\frac{b}{a} = c \qquad (6.105)$$

Putting value of constant (c) from equation (6.105) into equation (6.104), we get

$$\frac{1}{(a+b)}\ln\frac{(b+x)}{(a-x)} = k_1t + \frac{1}{(a+b)}\ln\frac{b}{a}$$

$$\frac{1}{(a+b)}\ln\frac{a(b+x)}{b(a-x)} = k_1t$$

$$\ln\frac{a(b+x)}{b(a-x)} = (a+b)k_1t \qquad (6.106)$$

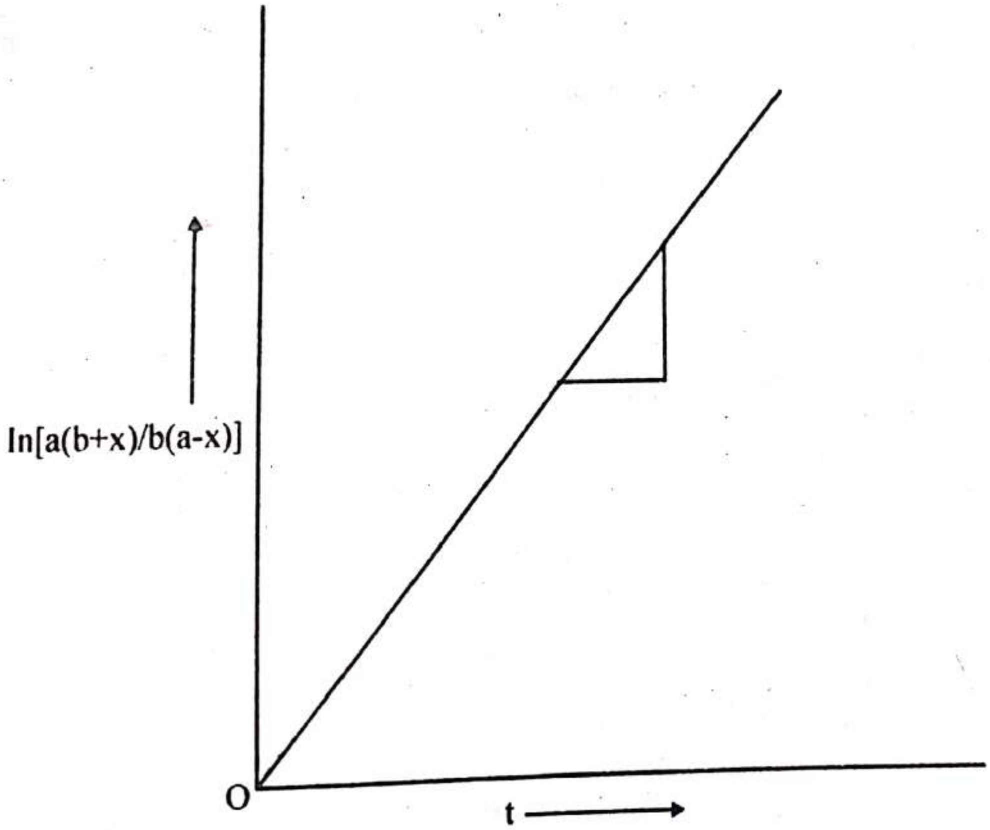


Fig. 6.27 Plot of ln[a(b+x)/b(a-x)] versus time for autocatalyst

Equation (6.106) is a straight line equation passing through the origin as shown in Fig. 6.27. Units of k_1 are $dm^3mol^{-1}s^{-1}$ and value of k_1 can be determined from the slope of the plot of ln [a(b+x)]/[b(a-x)] versus t as

$$\text{Slope} = k_1(a+b)$$

$$k_1 = \frac{\text{slope}}{(a+b)}$$

Case 3: Non-Autocatalyzed Reaction and Autocatalyzed Reactions as Parallel Reactions

In case 1 and 2 we considered only autocatalysis step of the reaction scheme. Here, we will discuss both steps of reaction scheme as parallel. Step (i) is simple 1st order reaction with rate constant k_1 and step (ii) is autocatalytic reaction with rate constant k_2.

$$A \xrightarrow{k_1} B + C \qquad \text{(Without catalyst)} \qquad \text{(i)}$$

$$A + B \xrightarrow{k_2} B + B + C \qquad \text{(Without catalyst)} \qquad \text{(ii)}$$

$$a \qquad 0 \qquad \text{when } t = 0$$

$$a-x \qquad x \qquad \text{when time} = t$$

Rate expression for the reaction (i) can be written as

$$R_1 \propto [A]$$

$$R_1 = k_1(a-x) \qquad (6.107)$$

Rate expression for reaction (ii) can be written as

$$R_2 \propto [A][B]$$

$$R_2 = k_2(a-x)(x) \qquad (6.108)$$

Overall rate of reaction is given as

$$\frac{dx}{dt} = R_1 + R_2$$

Putting values of R_1 and R_2 from equation (6.107) and (6.108) in above equation, we get

$$\frac{dx}{dt} = k_1(a-x) + k_2(a-x)(x)$$

$$\frac{dx}{dt} = (a-x)\{k_1 + k_2(x)\}$$

By separating variables and integrating above equation we get

$$\int \frac{dx}{(a-x)(k_1+k_2x)} = \int dt \qquad (6.109)$$

Using partial fractions,

$$\frac{1}{(a-x)(k_1+k_2x)} = \frac{A}{(a-x)} + \frac{B}{(k_1+k_2x)} \qquad (6.110)$$

$$1 = A(k_1+k_2x)+B(a-x) \qquad (6.111)$$

When a-x = 0, then x = a. Putting value of x in to equation (6.111), we get

$$1 = A(k_1+k_2a)$$

$$A = \frac{1}{(k_1+k_2a)} \qquad (6.112)$$

When $k_1+k_2x = 0$, then $x = -k_1/k$. Putting value of x into equation (6.111), we get

$$1 = B\left(a+\frac{k_1}{k_2}\right)$$

$$1 = B\left(\frac{k_2a+k_1}{k_2}\right)$$

$$B = \frac{k_2}{k_2a+k_1} \qquad (6.113)$$

From equations (6.112) and (6.113) putting the values of A and B in equation (6.110), we get

$$\frac{1}{(a-x)(k_1+k_2x)} = \frac{1}{(k_1+k_2a)(a-x)} + \frac{k_2}{(k_2a+k_1)(k_1+k_2x)}$$

$$\frac{dx}{(a-x)(k_1+k_2x)} = \frac{1}{(k_1+k_2a)}\left\{\frac{dx}{(a-x)} + \frac{k_2.dx}{(k_1+k_2x)}\right\}$$

$$\int\frac{dx}{(a-x)(k_1+k_2x)} = \frac{1}{(k_1+k_2a)}\left\{-\int\frac{(-1)dx}{(a-x)} + \int\frac{k_2.dx}{(k_1+k_2x)}\right\} \qquad (6.114)$$

By comparing equation (6.109) and (6.114), we get

$$\frac{1}{(k_1+k_2a)}\left\{-\int\frac{(-1)dx}{(a-x)} + \int\frac{k_2.dx}{(k_1+k_2x)}\right\} = \int dt$$

$$\frac{1}{(k_1+k_2a)}\{-\ln(a-x)+\ln(k_1+k_2x)\} = t+c$$

$$\frac{1}{(k_1+k_2a)}\left[\ln\frac{k_1+k_2x}{a-x}\right] = t+c \qquad (6.115)$$

Applying initial conditions,

When t = 0 then x = 0. Applying this condition at equation (6.115)

$$\frac{1}{(k_1+k_2a)}\ln\left(\frac{k_1}{a}\right)=c \tag{6.116}$$

Putting value of constant (c) from equation (6.116) into equation (6.115), we get

$$\frac{1}{(k_1+k_2a)}\left[\ln\frac{k_1+k_2x}{a-x}\right]=t+\frac{1}{(k_1+k_2a)}\ln\left(\frac{k_1}{a}\right)$$

$$\frac{1}{(k_1+k_2a)}\ln\frac{a(k_1+k_2x)}{k_1(a-x)}=t$$

$$\ln\frac{a(k_1+k_2x)}{k_1(a-x)}=(k_1+k_2a)t \tag{6.117}$$

Equation (6.117) is an equation of straight line passing through the origin with slope, (k_1+k_2a) as shown in Fig. 6.28.

From the slope value of rate constants k_1 and k_2 cannot be found. Hence, it is better to remove product from reaction mixture time to time. So, that no product remains in reaction mixture and process could not be autocatalyzed. So, $k_2 \approx 0$.

Applying this condition to equation (6.117), we get

$$\ln\frac{ak_1}{k_1(a-x)}=k_1t$$

$$\ln\frac{a}{(a-x)}=k_1t$$

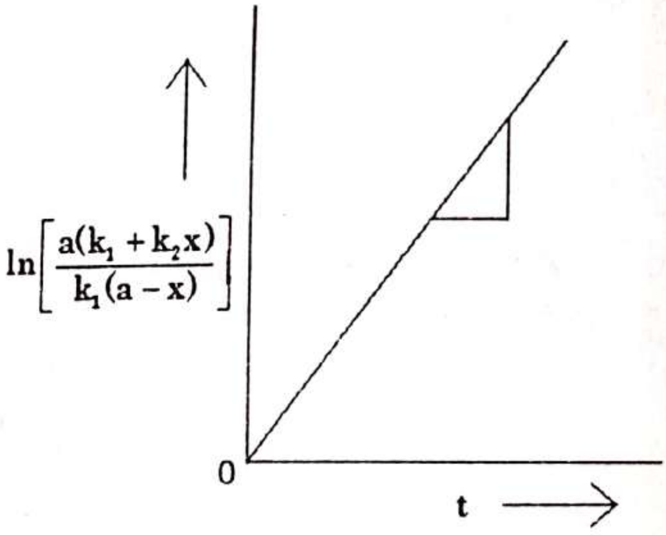


Fig. 6.28 Plot of $\ln\frac{a(k_1+k_2x)}{k_1(a-x)}$ versus t for non-autocatalyzed and autocatalyzed parallel reactions

Hence, from above equation k_1 can be found. By putting the value of k_1 in equation (6.117) we can get the value of k_2.

6.11.2 Enzyme Catalysis

Enzymes are bio organic catalysts which catalyze the chemical reactions occurring in the human body. Enzymes are macromolecules and proteins in nature, because they have origin in living organism so they are also called biopolymers. Amino acids are the building blocks of enzymes. Number of amino acids in a single enzyme is large so, 10000-1000000 g/mol is the molecular weight of enzyme. Enzymes act as catalyst in all types of reactions i.e. redox, acid base and decomposition reactions. Enzymes are specific in nature and functioning. Stereo specificity is basic character of enzymes. They react with stereo specific reactants and also produce stereo specific products. Enzymes only work on specific temperature and specific pH. Optimum pH or temperature is that pH or temperature at which enzyme show maximum activity. *"The number of reactant molecules converted into product per unit time by a single enzyme molecule is called turn over number."*

Michaelis-Menton Mechanism

Michaelis-Menton mechanism of enzyme catalysis obeys lock and key model of enzyme functionaing. An enzyme has specific site for adsorption of a particular substance. According to this model, substrate can form a complex with enzyme by a reversible process, then enzyme-substrate complex is converted into product with regeneration of enzyme by irreversible process. The pictorial diagram is shown in Fig. 6.29. The scheme of Michaelis-Menton mechanism of enzyme catalyzed reaction can be given as

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} ES \xrightarrow{k_2} E + P$$

According to above equation, rate of reaction is

$$\upsilon = k_2[ES] \qquad (6.118)$$

Net rate of formation of enzyme-substrate complex can be written as

$$\frac{d[ES]}{dt} = k_1[E][S] - k_{-1}[ES] - k_2[ES] \qquad (6.119)$$

Applying steady state approximation, because ES complex is formed and used during reaction and it is an unstable intermediate. So, d[ES]/dt = 0, equation (6.119) will be

$$0 = k_1[E][S] - k_{-1}[ES] - k_2[ES]$$

$$k_{-1}[ES] + k_2[ES] = k_1[E][S]$$

$$[ES]\{k_{-1} + k_2\} = k_1[E][S]$$

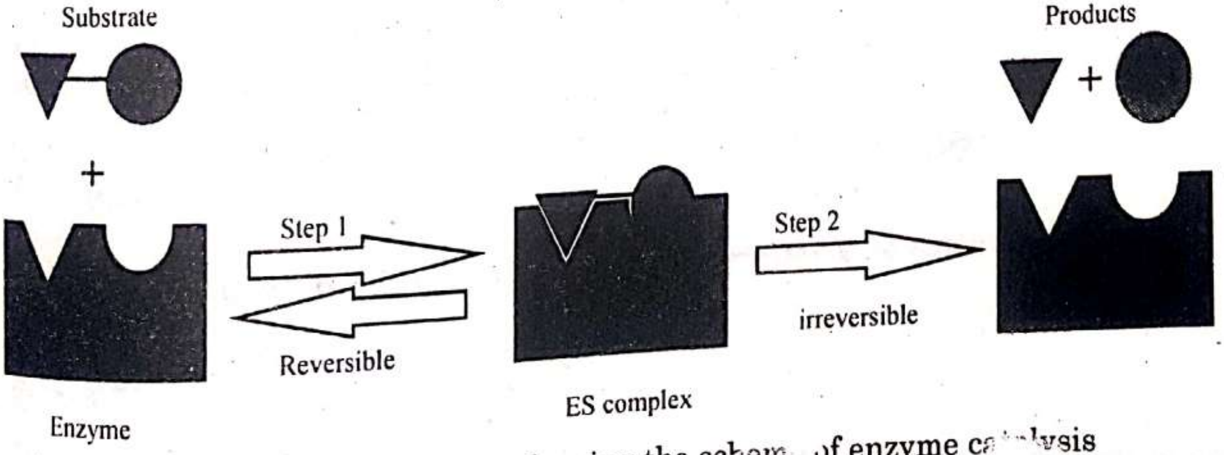


Fig. 6.29 Pictorial diagram showing the scheme of enzyme catalysis

$$[ES] = \frac{k_1[E][S]}{k_{-1} + k_2} \qquad (6.120)$$

Enzyme is present in a vessel in free form as well as in ES complex form. So,

$$[E]_o = [E] + [ES]$$

Where $[E]_o$ is the initial concentration of enzyme, [E] is the available concentration of free enzyme and [ES] is available concentration of enzyme substrate complex.

$$[E] = [E]_o - [ES] \qquad (6.121)$$

Putting value of [E] from equation (6.121) into equation (6.120), we get

$$[ES] = \frac{k_1\{[E]_o - [ES]\}[S]}{k_{-1} + k_2}$$

$$[ES] = \frac{\{[E]_o - [ES]\}[S]}{\frac{k_{-1} + k_2}{k_1}} \qquad (6.122)$$

$$k_M = \frac{k_{-1} + k_2}{k_1}$$

Where, k_M is the Michalis-Menton constant.

So, equation (6.122) will be

$$[ES] = \frac{[E]_o[S] - [ES][S]}{k_M}$$

$$[ES] = \frac{[E]_o[S]}{k_M} - \frac{[ES][S]}{k_M}$$

$$[ES] + \frac{[ES][S]}{k_M} = \frac{[E]_o[S]}{k_M}$$

$$[ES]\left[\frac{k_M + [S]}{k_M}\right] = \frac{[E]_o[S]}{k_M}$$

$$[ES] = \frac{[E]_o[S]}{k_M + [S]} \qquad (6.123)$$

Putting value of [ES] from equation (6.123) into (6.118), we get

$$\upsilon = k_2\frac{[E]_o[S]}{k_M + [S]} \qquad (6.124)$$

Results deduced from equation (6.124) are as follows

(i) Rate of reaction is a function of concentration of substrate.

(ii) Rate of reaction is directly proportional to [S] but up to certain limit only.

When [S] is low, then $k_M+[S] \approx k_M$ so, equation (6.124) will be

$$\upsilon = k_2 \frac{[E]_o[S]}{k_M}$$

$$\upsilon = \text{constant} \times [S]$$

$$\upsilon \propto [S]$$

So, rate of reaction is directly proportional to concentration of substrate if concentration of substrate is very low as shown in Fig. 6.30.

(iii) When [S] is very high, then $k_M+[S] \approx [S]$, applying this condition to equation (6.124), we get

$$\upsilon = k_2 \frac{[E]_o[S]}{[S]}$$

$$\upsilon = k_2[E]_o = \upsilon_{max}$$

υ_{max} is constant value, because k_2 and $[E]_o$ are constants. υ_{max} is independent of [S]. When $\upsilon = \upsilon_{max}/2$, then $[S] = k_M$. It means k_M is concentration of substrate when rate of reaction is half of maximum rate. Fig. 6.30 shows that υ is directly proportional to substrate concentration if concentration of substrate is low. But for high concentration of substrate υ is independent of [S].

This is because all the active sites of enzymes are fully occupied at high concentration of substrate and no more sites are available so, rate of reaction is independent of substrate concentration.

(iv) **Physical Significance of k_M:** "*k_M is the concentration of substrate for which rate of reaction is half of υ_{max}.*" i.e.

Let $[S] = k_M$ applying this condition on equation (6.124), we get

$$\upsilon = k_2 \frac{[E]_o k_M}{2k_M}$$

$$\upsilon = k_2 \frac{[E]_o}{2}$$

$$\upsilon = \frac{\upsilon_{max}}{2}$$

Unit of k_M are mol/dm³. As we know that

$$k_M = \frac{k_{-1} + k_2}{k_1}$$

$$k_M = \frac{k_{-1}}{k_1} + \frac{k_2}{k_1} \tag{6.125}$$

$k_s = \dfrac{k_{-1}}{k_1}$ is the dissociation constant so, equation (6.125) will be

$$k_M = k_s + \frac{k_2}{k_1}$$

If $k_2/k_1 = 0$ then $k_M = k_s$. The value of k_s normally ranges 10^{-2} to 10^{-5} mol/dm^3 which is comparable to ionization constant of carboxylic acids. Generally $k_M \leq k_s$, so k_M can serve as minimum value of k_s.

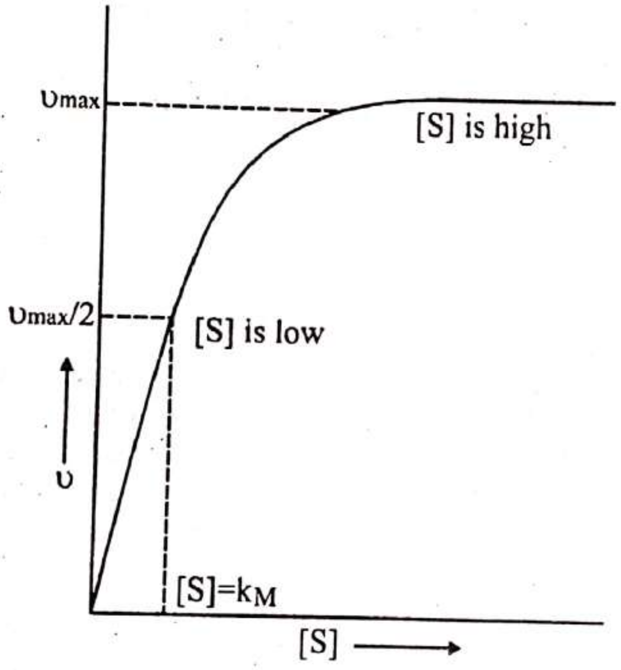


Fig. 6.30 Plot of rate of enzyme catalyzed reaction versus substrate concentration

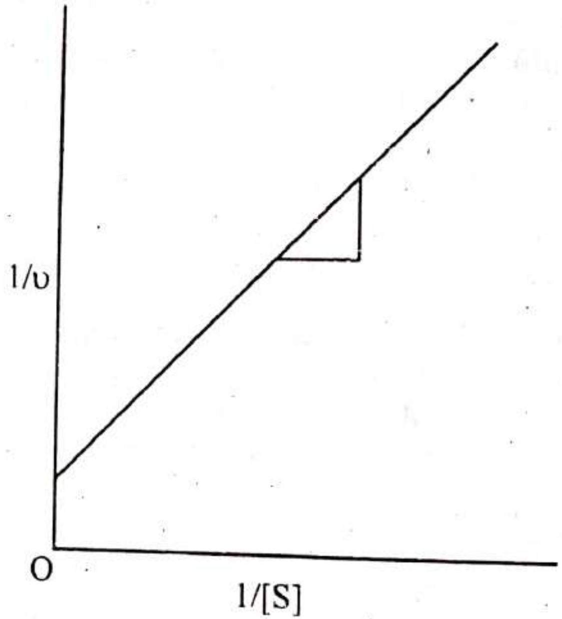


Fig. 6.31 Plot of 1/v versus 1/[S]

(v) The value of k_M and k_2 can be determine by converting equation (6.124) into equation of straight line i.e.

$$\upsilon = \frac{k_2[E]_o[S]}{k_M + [S]}$$

$$\frac{1}{\upsilon} = \frac{k_M + [S]}{k_2[E]_o[S]}$$

$$\frac{1}{\upsilon} = \frac{k_M}{k_2[E]_o[S]} + \frac{[S]}{k_2[E]_o[S]}$$

$$\frac{1}{\upsilon} = \frac{k_M}{k_2[E]_o[S]} + \frac{1}{k_2[E]_o}$$

$$\frac{1}{\upsilon} = \frac{k_M}{k_2[E]_o}\frac{1}{[S]} + \frac{1}{k_2[E]_o}$$

This is an equation of straight line and named as Line weaver burk plot as shown in Fig. 6.31. The value of k_M can be determined from the slope of $1/\upsilon$ versus $1/[S]$ plot and k_2 from the intercept of the same plot as

$$\text{Slope} = \frac{k_M}{k_2[E]_o}$$

$$\text{Intercept} = \frac{1}{k_2[E]_o}$$

$$\frac{1}{k_2} = [E]_o \times \text{Intercept}$$

$$k_2 = 1/\,[E]_o \times \text{Intercept}$$

The rate of slope to intercept also gives the value of k_M.

$$\frac{\text{Slope}}{\text{Intercept}} = \frac{k_M}{k_2[E]_o}$$

$$\frac{\text{Slope}}{\text{Intercept}} = k_M$$

Second Possible Mechanism of Enzyme Catalysis

The Michaelis-Menton plot doesn't always show that this mechanism is true, because many other possible mechanisms can give this plot. For example stepwise formation of product from ES complex follows the equation almost similar to Michaelis-Menton equation discussed in the previous section. Pictorial diagram of this mechanism is given in Fig. 6.32.

The scheme of this mechanism can be written as

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} ES$$

$$ES \xrightarrow{k_2} ES' + X$$

$$ES' \xrightarrow{k_3} E + Y$$

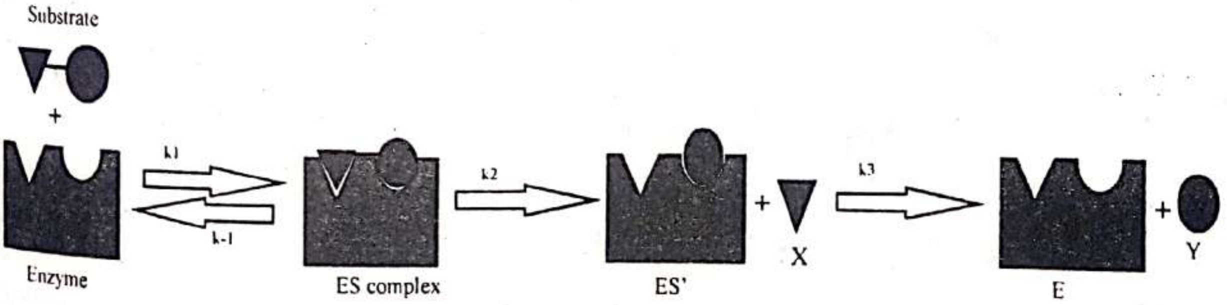


Fig. 6.32 Pictorial diagram of mechanism of enzyme catalyzed reaction

Rate of reaction is directly proportional to concentration of ES complex.

$$\upsilon \propto [\mathrm{ES}]$$

$$\upsilon = k_2[\mathrm{ES}] \tag{6.126}$$

k_2 is the rate constant of second step.

Net rate of formation of ES complex is

$$\frac{d[\mathrm{ES}]}{dt} = k_1[\mathrm{E}][\mathrm{S}] - k_{-1}[\mathrm{ES}] - k_2[\mathrm{ES}]$$

Applying steady state approximation, we get

$$0 = k_1[\mathrm{E}][\mathrm{S}] - [\mathrm{ES}]\{k_{-1} + k_2\}$$

$$[\mathrm{ES}]\{k_{-1} + k_2\} = k_1[\mathrm{E}][\mathrm{S}]$$

$$[\mathrm{ES}] = \frac{k_1[\mathrm{E}][\mathrm{S}]}{k_{-1} + k_2}$$

$$[\mathrm{ES}] = \frac{[\mathrm{E}][\mathrm{S}]}{\dfrac{k_{-1} + k_2}{k_1}}$$

$$[\mathrm{ES}] = \frac{[\mathrm{E}][\mathrm{S}]}{k_M} \tag{6.127}$$

Enzyme is present in free as well as in enzyme-substrate complex forms in reaction mixture. Thus total concentration of enzyme is equal to sum of concentration of all these three forms as

$$[\mathrm{E}]_0 = [\mathrm{E}] + [\mathrm{ES}] + [\mathrm{ES'}]$$

$$[\mathrm{E}] = [\mathrm{E}]_0 - [\mathrm{ES}] - [\mathrm{ES'}] \tag{6.128}$$

Putting value of [E] from equation (6.128) into (6.127), we get

$$[\mathrm{ES}] = \frac{\{[\mathrm{E}]_0 - [\mathrm{ES}] - [\mathrm{ES'}]\}[\mathrm{S}]}{k_M}$$

$$[\mathrm{ES}] + \frac{[\mathrm{ES}][\mathrm{S}]}{k_M} = \frac{\{[\mathrm{E}]_0 - [\mathrm{ES'}]\}[\mathrm{S}]}{k_M}$$

$$[\mathrm{ES}] + \frac{[\mathrm{ES}][\mathrm{S}]}{k_M} = \frac{[\mathrm{E}]_0[\mathrm{S}] - [\mathrm{ES'}][\mathrm{S}]}{k_M}$$

$$\frac{k_M[\mathrm{ES}] + [\mathrm{ES}][\mathrm{S}]}{k_M} = \frac{[\mathrm{E}]_0[\mathrm{S}] - [\mathrm{ES'}][\mathrm{S}]}{k_M}$$

$$[\mathrm{ES}]\left(k_M + [\mathrm{S}]\right) = [\mathrm{E}]_0[\mathrm{S}] - [\mathrm{ES'}][\mathrm{S}] \tag{6.129}$$

Net rate of formation of ES′

$$\frac{d[ES']}{dt} = k_2[ES] - k_3[ES'] \qquad (6.130)$$

As ES′ is also an intermediate. So, steady state approximation can also be applied to it.

$$0 = k_2[ES] - k_3[ES']$$

$$k_2[ES] = k_3[ES']$$

$$[ES'] = \frac{k_2[ES]}{k_3} \qquad (6.131)$$

Putting value of [ES′] from equation (6.131) into equation (6.129), we get

$$[ES](k_M + [S]) = [E]_o[S] - \frac{k_2[ES]}{k_3}[S]$$

$$[ES](k_M + [S]) + \frac{k_2[ES][S]}{k_3} = [E]_o[S]$$

$$[ES]\left\{k_M + [S] + \frac{k_2[S]}{k_3}\right\} = [E]_o[S]$$

$$[ES]\left\{k_M + \left(1 + \frac{k_2}{k_3}\right)[S]\right\} = [E]_o[S] \qquad (6.132)$$

$$[ES]\left\{k_M + \left(\frac{k_3 + k_2}{k_3}\right)[S]\right\} = [E]_o[S]$$

$$[ES] = \frac{[E]_o[S]}{k_M + \left(\frac{k_3 + k_2}{k_3}\right)[S]} \qquad (6.133)$$

Putting value of [ES] from equation (6.133) into (6.126), we get

$$\upsilon = \frac{k_2[E]_o[S]}{k_M + \left(\frac{k_3 + k_2}{k_3}\right)[S]}$$

$$\upsilon = \frac{k_2\left(\frac{k_3}{k_2 + k_3}\right)[E]_o[S]}{\left(\frac{k_3}{k_2 + k_3}\right)k_M + \left(\frac{k_3 + k_2}{k_3}\right)\left(\frac{k_3}{k_2 + k_3}\right)[S]}$$

$$\upsilon = \frac{k_2\left(\dfrac{k_3}{k_2+k_3}\right)[E]_o[S]}{\left(\dfrac{k_3}{k_2+k_3}\right)k_M+[S]} \qquad (6.134)$$

And $\quad k = \left(\dfrac{k_3}{k_2+k_3}\right)$

So, equation (6.134) will be,

$$\upsilon = \frac{k_2 k[E]_o[S]}{k_M k+[S]} \qquad (6.135)$$

$k_3 >>>> k_2$ then $k = 1$. This is a maximum value of k.

Results deduced from equation (6.135) are as follows

(i) Rate of enzyme catalyzed reaction is directly proportional to substrate concentration for small values of [S]. i.e.

(a) If [S] is low, then $k_M.k + [S] \approx k_M.k$

Applying this condition to equation (6.135), we get

$$\upsilon = \frac{k_2 k[E]_o[S]}{k_M k}$$

Hence, $\upsilon \propto [S]$

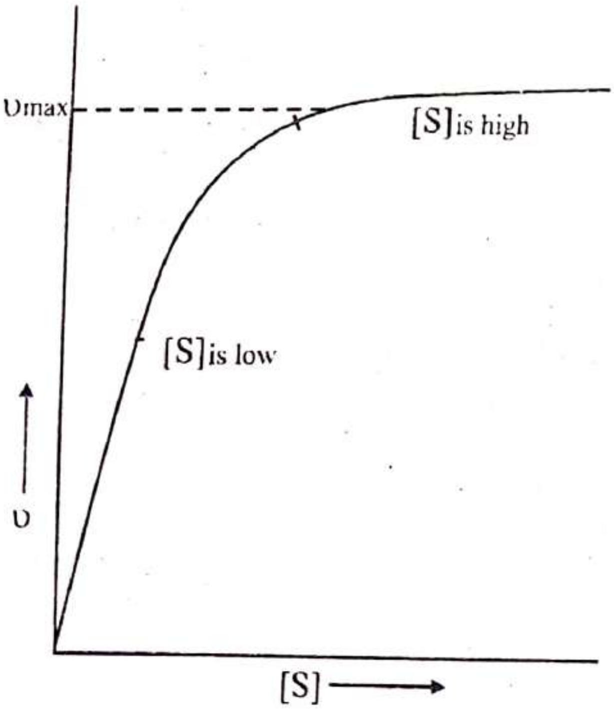


Fig. 6.33 Plot of rate of enzyme catalyzed reaction versus substrate concentration

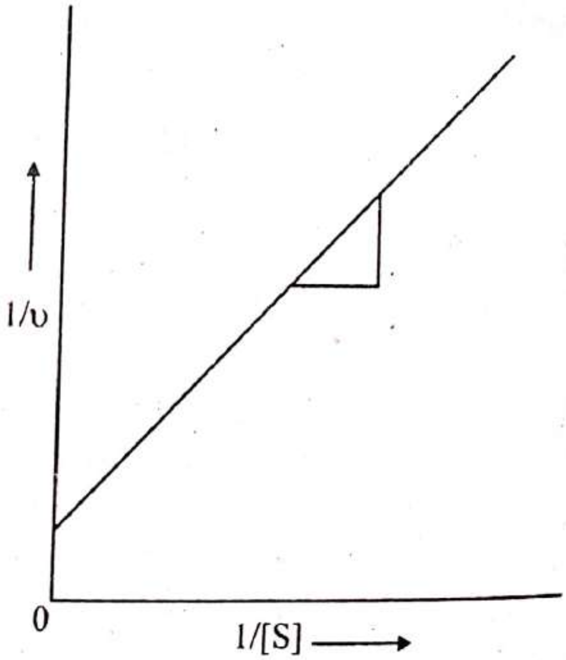


Fig. 6.34 Plot of 1/v versus 1/[S]

(b) When value of [S] is high then υ is independent of [S] i.e. if [S] is large, then $k_M.k + [S] \approx [S]$ so, equation (6.135) will be

$$\upsilon = k_2 k[E]_0$$

Fig. 6.33 depicts that rate of enzyme catalyzed reaction depends upon substrate at low concentration but at high substrate concentration rate becomes independent of substrate concentration.

(ii) The value of k_M can be determined by converting equation (6.135) into equation of straight line i.e.

Taking inverse of equation (6.135), we get

$$\frac{1}{\upsilon} = \frac{k_M k + [S]}{k_2 k[E]_0 [S]}$$

$$\frac{1}{\upsilon} = \frac{k_M}{k_2 [E]_0 [S]} + \frac{1}{k_2 k[E]_0}$$

This is equation of straight line with intercept as shown in Fig. 6.34. The ratio of slope to intercept of the plot of $1/\upsilon$ as a function of $1/[S]$ can be used for the determination of k_M.

6.12 ENZYME INHIBITION

"The decrease in rate of enzyme catalyzed reaction as a result of complex formation of a foreign substance with enzyme is called enzyme inhibition and foreign specie is called inhibitor."

Types of Enzyme Inhibition

Reversible and irreversible are two types of enzyme inhibition. Reversible inhibition is further classified into three types.

(i) Competitive inhibition

(ii) Un competitive inhibition

(iii) Non–competitive inhibition

6.12.1 Competitive Inhibition

In this inhibition, there are complexations between substrate and enzyme and between enzyme and foreign specie. In competitive inhibition enzyme has ability to bind with substrate as well as with inhibitor because size and shape of inhibitor and substrate are not only same and but also similar to active site.

The scheme of competitive inhibition can be written as

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} ES \xrightarrow{k_2} P + E$$

The complexation of enzyme with inhibitor is a reversible process and can be written as

$$E + I \rightleftharpoons EI$$

From above equilibrium, dissociation constant of the complex is

$$K_I = \frac{[E][I]}{[EI]}$$

By rearranging above equation, we get

$$[EI] = \frac{[E][I]}{K_I} \tag{6.136}$$

Rate of reaction is directly proportional to available concentration of enzyme substrate complex.

$$\upsilon \propto [ES]$$

$$\upsilon = k_2[ES] \tag{6.137}$$

Net rate of formation of $[ES]=R_{\text{formation}} - R_{\text{consumption}}$

$$\frac{d[ES]}{dt} = k_1[E][S] - k_{-1}[ES] - k_2[ES]$$

Applying steady state approximation to it

$$0 = k_1[E][S] - k_{-1}[ES] - k_2[ES]$$

$$k_1[E][S] = k_{-1}[ES] + k_2[ES]$$

$$k_1[E][S] = (k_2 + k_{-1})[ES]$$

$$[ES] = \frac{k_1[E][S]}{k_2 + k_{-1}}$$

$$[ES] = \frac{[E][S]}{\frac{k_2 + k_{-1}}{k_1}}$$

$$[ES] = \frac{[E][S]}{k_M}$$

$$[E] = \frac{[ES]k_M}{[S]} \tag{6.138}$$

The concentration of enzyme is as follows

$$[E]_o = [E] + [ES] + [EI] \tag{6.139}$$

Putting value of [EI] from equation (6.136) into (6.139), we get

$$[E]_o = [E] + [ES] + \frac{[E][I]}{K_I}$$

$$[E]_0 = [ES] + [E]\left\{1 + \frac{[I]}{K_I}\right\} \qquad (6.140)$$

Putting value of [E] from equation (6.138) into equation (6.140), we get

$$[E]_0 = [ES] + \frac{[ES]k_M}{[S]}\left\{1 + \frac{[I]}{K_I}\right\}$$

$$[E]_0 = [ES]\left(1 + \frac{k_M}{[S]}\left\{1 + \frac{[I]}{K_I}\right\}\right)$$

$$[ES] = \frac{[E]_0}{\left(1 + \frac{k_M}{[S]}\left\{1 + \frac{[I]}{K_I}\right\}\right)} \qquad (6.141)$$

Putting value of [ES] from equation (6.141) into (6.137), we get

$$\upsilon = k_2 \frac{[E]_0}{\left(1 + \frac{k_M}{[S]}\left\{1 + \frac{[I]}{K_I}\right\}\right)}$$

This is the rate of enzyme catalyzed reaction in the presence of inhibitor.

$$\upsilon = \frac{k_2[E]_0[S]}{\left([S] + k_M\left\{1 + \frac{[I]}{K_I}\right\}\right)} \qquad (6.142)$$

Equation (6.142) proves that υ decreases with increase in [I] and increases with increase in [S] i.e.

(i) If [I] = 0, then equation (6.142) will be

$$\upsilon = \frac{k_2[E]_0[S]}{[S] + k_M}$$

This is rate of enzyme catalyzed reaction in the absence of inhibitor.

(ii) If $[I]/K_I=1$ and $k_M=[S]$, then

$$\upsilon = \frac{k_2[E]_0}{3}$$

$$\upsilon = \frac{\upsilon_{max}}{3}$$

(iii) If $[I]/K_I = 0$ and $k_M = [S]$, then equation (6.142) will be

$$\upsilon = \frac{k_2[E]_0}{2}$$

$$\upsilon = \frac{\upsilon_{max}}{2}$$

This is in the absence of inhibitor as shown in Fig. 6.35.

(iv) If [S] >>>>k_M, then equation (6.142) is

$$\upsilon = \frac{k_2[E]_o[S]}{[S]}$$

$$\upsilon = k_2[E]_o$$

$$\upsilon = \upsilon_{max}$$

By taking inverse of equation (6.142), we get

$$\frac{1}{\upsilon} = \frac{[S] + k_M\left\{1 + \frac{[I]}{K_I}\right\}}{k_2[E]_o[S]}$$

$$\frac{1}{\upsilon} = \frac{1}{k_2[E]_o} + \frac{k_M\left\{1 + \frac{[I]}{K_I}\right\}}{k_2[E]_o[S]}$$

$$\frac{1}{\upsilon} = \frac{k_M}{k_2[E]_o}\left(1 + \frac{[I]}{K_I}\right)\frac{1}{[S]} + \frac{1}{k_2[E]_o} \qquad (6.143)$$

Plot of equation (6.143) is shown in Fig. 6.36.

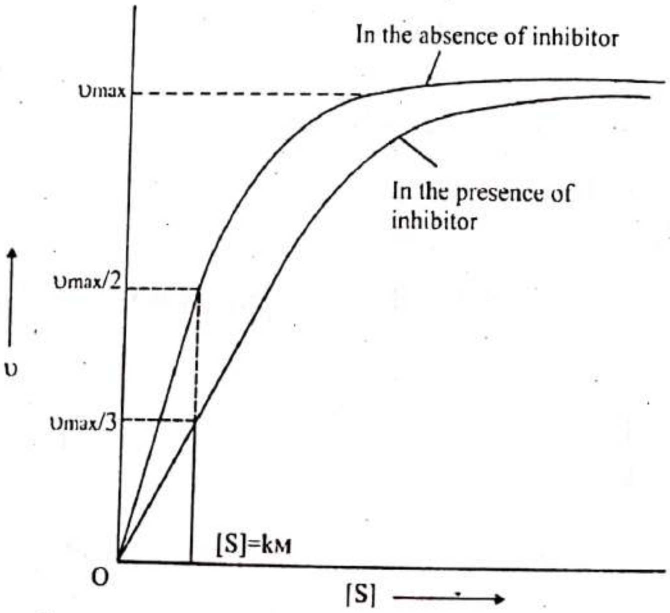


Fig. 6.35 The rate of enzyme catalyzed reaction as a function of substrate concentration in the presence and absence of inhibitor

With the increase in [I] the curve will shift anti clockwise with increasing slope and intercept will remain constant.

$$\text{Intercept} = \frac{1}{k_2[E]_o}$$

$$k_2 = \frac{1}{\text{Intercept}[E]_o}$$

$$\text{Slope} = \frac{k_M}{k_2[E]_o}\left(1 + \frac{[I]}{K_I}\right)$$

Then, we can find K_I from slope.

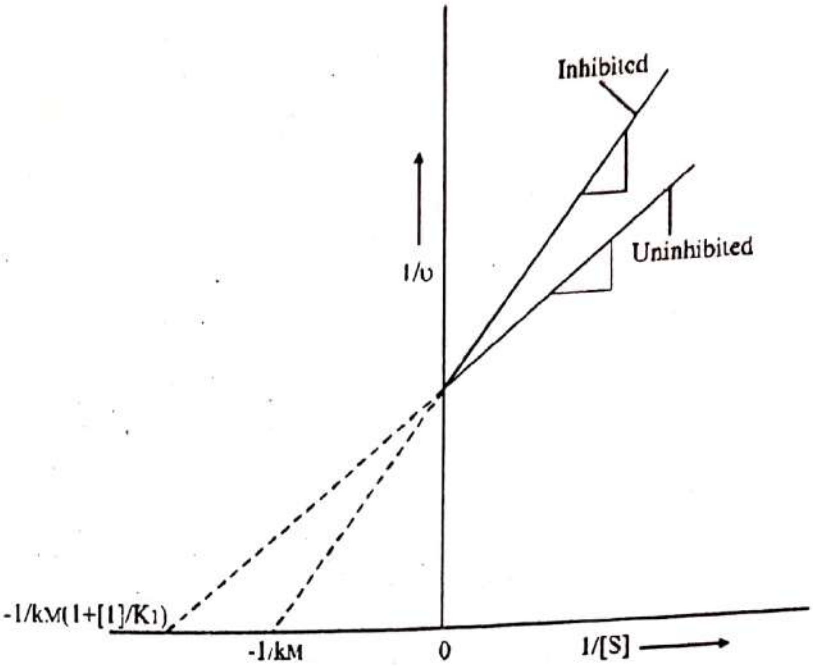


Fig. 6.36 Plot of 1/υ as a function of 1/[S] in the presence (competitive inhibition) and absence of inhibitor

Example 6.5

Prove that the value of x-intercept of the plot 1/υ versus 1/[S] is equal to

$$-\frac{1}{k_M\left(1 + \frac{[I]}{K_I}\right)}$$

Solution

x- Intercept of 1/υ versus 1/[S] plot is the value of 1/[S] for which 1/υ is equal to zero. Hence, from equation (6.143) we have

$$0 = \frac{k_M}{k_2[E]_o}\left(1 + \frac{[I]}{K_I}\right)\frac{1}{[S]} + \frac{1}{k_2[E]_o}$$

$$-\frac{k_M}{k_2[E]_o}\left(1 + \frac{[I]}{K_I}\right)\frac{1}{[S]} = \frac{1}{k_2[E]_o}$$

$$\frac{1}{[S]} = -\frac{1}{k_M\left(1 + \frac{[I]}{K_I}\right)}$$

As required.

Example 6.6

An enzyme catalyzed reaction was inhibited competitively. The intercept to slope ratio of plot 1/υ versus 1/[S] was found to be 1.5 mol/dm³ in the presence of 0.01 M inhibitor. The value of k_M is 1.2×10^{-4} moldm^{-3}. Calculate the value of K_I.

Solution

As we know that, $$\frac{\text{Intercept}}{\text{Slope}}=\frac{k_M}{k_2[E]_o}\left(1+\frac{[I]}{K_I}\right)\times k_2[E]_o$$

$$\frac{\text{Intercept}}{\text{Slope}}=k_M\left(1+\frac{[I]}{K_I}\right)$$

By putting values in above equation from the given data we can determine value of K_I as follows

$$1.5=1.2\times10^{-4}\left(1+\frac{0.01}{K_I}\right)$$

$$1.25\times10^{4}=1+\frac{0.01}{K_I}$$

$$K_I=7.999\ \text{mol dm}^{-3}$$

6.12.2 Uncompetitive Inhibition

In such type of inhibition, enzyme doesn't make a complex with inhibitor directly but enzyme-substrate form a complex with inhibitor and stabilize it. As a result of this process product formation is inhibited. The scheme of uncompetitive inhibition is given below

$$E+S\underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}}ES\xrightarrow{k_2}E+P$$

$$ES+I\underset{\text{Dissociation}}{\overset{\text{Association}}{\rightleftharpoons}}ESI$$

Dissociation constant of [ESI] will be

$$K_I=\frac{[ES][I]}{[ESI]}$$

$$[ESI]=\frac{[ES][I]}{K_I}\tag{6.144}$$

$$\upsilon\propto[ES]$$

$$\upsilon=k_2[ES]\tag{6.145}$$

Net rate of formation of [ES] complex

$$\frac{d[ES]}{dt}=k_1[E][S]-k_{-1}[ES]-k_2[ES]$$

Applying steady state approximation to it

$$0=k_1[E][S]-k_{-1}[ES]-k_2[ES]$$

$$k_1[E][S] = k_{-1}[ES] + k_2[ES]$$

$$k_1[E][S] = (k_2 + k_{-1})[ES]$$

$$[ES] = \frac{k_1[E][S]}{k_2 + k_{-1}}$$

$$[ES] = \frac{[E][S]}{\frac{k_2 + k_{-1}}{k_1}}$$

$$[ES] = \frac{[E][S]}{k_M} \qquad (6.146)$$

$$[E]_o = [E] + [ES] + [ESI]$$

$$[E] = [E]_o - [ES] - [ESI] \qquad (6.147)$$

By putting value of [ESI] from equation (6.144) into equation (6.147), we get

$$[E] = [E]_o - [ES] - \frac{[ES][I]}{K_I}$$

Putting value of [E] into equation (6.146), we get

$$[ES] = \frac{\left([E]_o - [ES] - \frac{[ES][I]}{K_I}\right)[S]}{k_M}$$

$$[ES]k_M = \left([E]_o - [ES] - \frac{[ES][I]}{K_I}\right)[S]$$

$$[ES]k_M = \left([E]_o - [ES]\left\{1 + \frac{[I]}{K_I}\right\}\right)[S]$$

$$[ES]k_M = [E]_o[S] - [ES][S]\left\{1 + \frac{[I]}{K_I}\right\}$$

$$[ES]k_M + [ES][S]\left\{1 + \frac{[I]}{K_I}\right\} = [E]_o[S]$$

$$[ES]\left(k_M + [S]\left\{1 + \frac{[I]}{K_I}\right\}\right) = [E]_o[S]$$

$$[ES] = \frac{[E]_o[S]}{k_M + [S]\left\{1 + \frac{[I]}{K_I}\right\}} \qquad (6.148)$$

Putting value of [ES] from equation (6.145) into equation (6.148), we get

$$\upsilon = k_2 \frac{[E]_o[S]}{k_M + [S]\left\{1 + \frac{[I]}{K_I}\right\}} \tag{6.149}$$

It is the rate law expression of enzyme catalyzed reaction in the presence of inhibitor due to uncompetitive inhibition.

Taking inverse of equation (6.149)

$$\frac{1}{\upsilon} = \frac{k_M + [S]\left\{1 + \frac{[I]}{K_I}\right\}}{k_2[E]_o[S]}$$

$$\frac{1}{\upsilon} = \frac{k_M}{k_2[E]_o}\frac{1}{[S]} + \frac{1}{k_2[E]_o}\left\{1 + \frac{[I]}{K_I}\right\} \tag{6.150}$$

This is the rate law expression for enzyme catalyzed reaction suffering uncompetitive inhibition. We can know that the inhibition is competitive or uncompetitive by Line weaver Burk Plot. If intercept is same but slope is different in Line weaver Burk plot then this will be competitive inhibition. If intercept is different and slope will be same in Line weaver Burk plot then this will be uncompetitive inhibition as shown in Fig. 6.37.

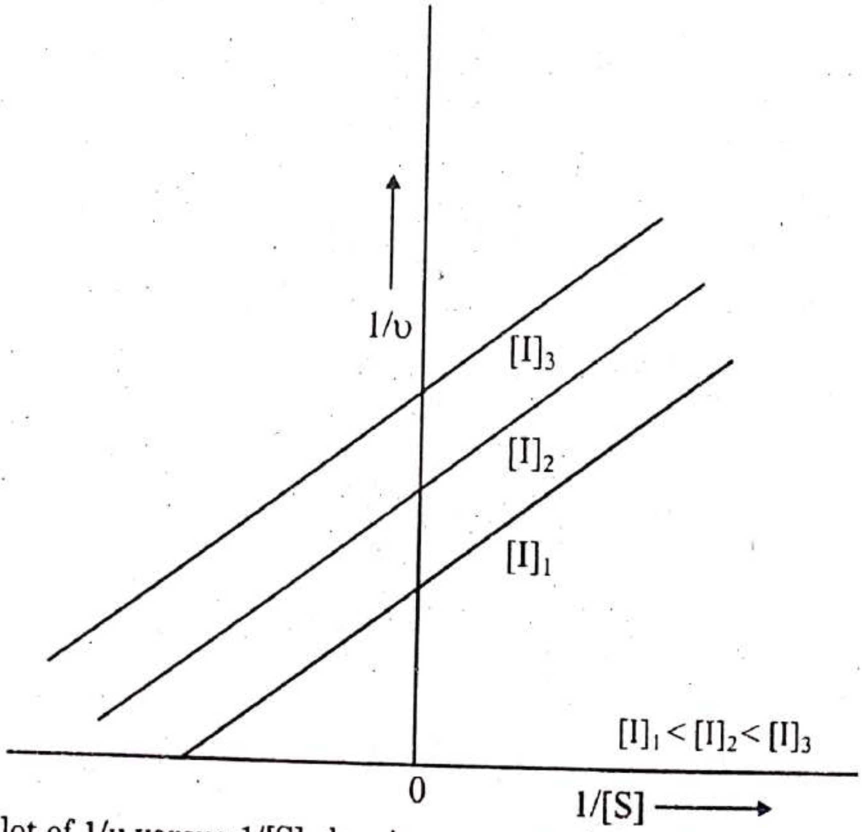


Fig. 6.37 Plot of 1/υ versus 1/[S] showing uncompetitive inhibition with different intercept values

6.12.3 Non-Competitive Inhibition

In this type of enzyme inhibition, inhibitor is not attached with enzyme through active site. Inhibitor forms complex with enzyme by attaching active site available for substrate. Because shape and size of inhibitor and of substrate are different from each other. The reaction scheme of non-competitive inhibition is given below

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES \xrightarrow{k_2} E + P$$

$$E + I \underset{K_I}{\rightleftharpoons} EI \text{ (Possibility 1)}$$

$$ES + I \underset{K_I}{\rightleftharpoons} ESI \text{ (Possibility 2)}$$

Dissociation constant of possibility 1 is

$$K_I = \frac{[E][I]}{[EI]}$$

$$[EI] = \frac{[E][I]}{K_I} \qquad (6.151)$$

Dissociation constant of possibility 2 is

$$K_I = \frac{[ES][I]}{[ESI]}$$

$$[ESI] = \frac{[ES][I]}{K_I} \qquad (6.152)$$

$$\upsilon = k_2[ES] \qquad (6.153)$$

Net rate of formation of [ES] complex

$$\frac{d[ES]}{dt} = k_1[E][S] - k_{-1}[ES] - k_2[ES]$$

Applying steady state approximation to it

$$0 = k_1[E][S] - k_{-1}[ES] - k_2[ES]$$

$$k_1[E][S] = k_{-1}[ES] + k_2[ES]$$

$$k_1[E][S] = (k_2 + k_{-1})[ES]$$

$$[ES] = \frac{k_1[E][S]}{k_2 + k_{-1}}$$

$$[ES] = \frac{[E][S]}{\frac{k_2 + k_{-1}}{k_1}}$$

$$[ES] = \frac{[E][S]}{k_M} \tag{6.154}$$

Initial concentration of enzyme should be equal to the sum of various forms of enzyme concentration.

$$[E]_o = [E] + [ES] + [EI] + [ESI] \tag{6.155}$$

Putting value of [ES] from equation (6.154) into equation (6.155)

$$[E]_o = [E] + \frac{[E][S]}{k_M} + [EI] + [ESI] \tag{6.156}$$

Putting values of [EI] and [ESI] from equation (6.151) and (6.152) into equation (6.156), we get

$$[E]_o = [E] + \frac{[E][S]}{k_M} + \frac{[E][I]}{K_I} + \frac{[ES][I]}{K_I}$$

$$[E]_o = [E] + \frac{[E][S]}{k_M} + \frac{[E][I]}{K_I} + \frac{[E][S]}{k_M}\frac{[I]}{K_I}$$

$$[E]_o = [E]\left(1 + \frac{[S]}{k_M} + \frac{[I]}{K_I} + \frac{[S][I]}{k_M K_I}\right)$$

$$[E] = \frac{[E]_o}{\left(1 + \frac{[S]}{k_M} + \frac{[I]}{K_I} + \frac{[S][I]}{k_M K_I}\right)}$$

Now putting value of [E] from above equation into equation (6.154)

$$[ES] = \frac{[S]}{k_M}\frac{[E]_o}{\left(1 + \frac{[S]}{k_M} + \frac{[I]}{K_I} + \frac{[S][I]}{k_M K_I}\right)}$$

Putting value of [ES] into equation (6.153), we get

$$\upsilon = \frac{k_2[E]_o[S]}{k_M\left(1 + \frac{[S]}{k_M} + \frac{[I]}{K_I} + \frac{[S][I]}{k_M K_I}\right)}$$

$$\upsilon = \frac{k_2[E]_o[S]}{\left(k_M + k_M\frac{[I]}{K_I} + [S] + \frac{[S][I]}{K_I}\right)}$$

$$\upsilon = \frac{k_2[E]_o[S]}{k_M\left(1 + \frac{[I]}{K_I}\right) + [S]\left(1 + \frac{[I]}{K_I}\right)} \tag{6.157}$$

Taking inverse of equation (6.157), we get

$$\frac{1}{\upsilon}=\frac{k_M}{k_2[E]_o}\left(1+\frac{[I]}{K_I}\right)\frac{1}{[S]}+\frac{1}{k_2[E]_o}\left(1+\frac{[I]}{K_I}\right) \qquad (6.158)$$

Equation (6.158) is an equation of straight line with intercept form.

$$\text{Slope}=\frac{k_M}{k_2[E]_o}\left(1+\frac{[I]}{K_I}\right)$$

$$\text{Intercept}=\frac{1}{k_2[E]_o}\left(1+\frac{[I]}{K_I}\right)$$

[I] is present in slope and intercept so, by changing [I] the y-intercept and slope will change, but x-intercept remains constant. The plot will be different from competitive and uncompetitive inhibition in which one thing remains constant either slope or intercept but in this case both are variable as shown in Fig. 6.38.

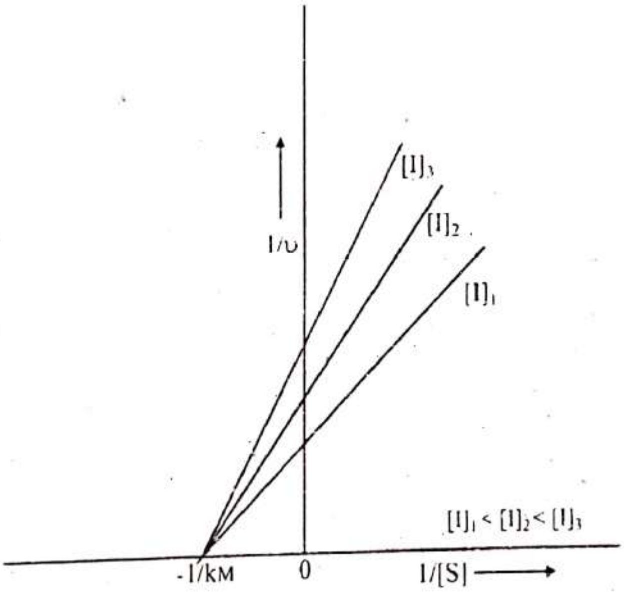


Fig. 6.38 Plot of 1/υ versus 1/[S] in case of non-competitive inhibition

Example 6.7

Prove that the value of x-intercept of the plot of 1/υ vs. 1/[S] is equal to $-\frac{1}{k_M}$.

Solution

x-intercept of 1/υ versus 1/[S] plot is the value of 1/[S] for which 1/ υ is equal to zero so, from equation (6.158)we have,

$$0=\frac{k_M}{k_2[E]_o}\left(1+\frac{[I]}{K_I}\right)\frac{1}{[S]}+\frac{1}{k_2[E]_o}\left(1+\frac{[I]}{K_I}\right)$$

$$-\frac{k_M}{k_2[E]_o}\left(1+\frac{[I]}{K_I}\right)\frac{1}{[S]}=\frac{1}{k_2[E]_o}\left(1+\frac{[I]}{K_I}\right)$$

$$-k_M\left(1+\frac{[I]}{K_I}\right)\frac{1}{[S]}=\left(1+\frac{[I]}{K_I}\right)$$

$$\frac{1}{[S]}=-\frac{1}{k_M}$$

Hence, it has been proved that $1/[S]$ is equal to $-1/k_M$.

6.13 B.E.T EQUATION

The various types of adsorption isotherms could not be explained by mono-molecular layer adsorption theory of Langmuir, Brunauer, Emett and Teller developed a theory of multi-molecular layer adsorption of gases and vapours. This theory is known as B.E.T theory. These workers extended Langmuir theory to multi-layer adsorption and derived a mathematical equation called B.E.T equation or B.E.T isotherm, which explained satisfactorily all the five types of experimental adsorption isotherms.

Postulates of B.E.T Theory

This theory is based upon the following assumptions

(i) Adsorption involves the formation of multi-molecular layer, rather than mono-molecular layer. This is represented as follows

$$\text{Vapour} + \text{Free surface} \rightleftharpoons \text{Single complexes}$$

$$\text{Vapour} + \text{Single complexes} \rightleftharpoons \text{Double complexes}$$

$$\text{Vapour} + \text{Double complexes} \rightleftharpoons \text{Tripple complexes, etc.}$$

(ii) Langmuir's idea of fixed (localized) adsorption sites was retained.

(iii) The interactions between the adsorbate molecules in the adsorption layer were neglected.

(iv) For the formation of single complexes, the assumption made in Langmuir's theory is adopted.

(v) There is dynamic equilibrium between the successive layers. The rate of evaporation (desorption) from the first layer is equal to the rate of condensation on the preceeding layer.

(vi) The forces that produce consideration are responsible for binding energy in successive multilayers.

(vii) Heat of adsorption of first layer is different from that of subsequent layers.

(viii) After the first layer, the heat of adsorption is equal to heat of condensation of vapours.

(ix) Adsorption and desorption occur on surface only.

Statement of B.E.T Equation

On the basis of above postulates, Brunauer, Emmett and Teller derived the following equation

$$\frac{p}{V(p^{o}-p)}=\frac{1}{V_{m}C}+\left(\frac{C-1}{V_{m}C}\right)\frac{p}{p^{o}} \tag{6.159}$$

This equation is called B.E.T equation. In this equation

Here V is volume, reduced to standard conditions of the gas adsorbed at pressure p and temperature T, p^{o} is saturated vapour pressure of adsorbate (gas or vapour) at temperature T and V_m is volume of gas, reduced to standard conditions (i.e. at NTP), adsorbed to form a saturated monolayer per gram of the adsorbent. While C is a constant equal to $e^{(E_1-E_L)/RT}$ at any given temperature. Here E_1 is heat of adsorption of first layer. E_L is heat of condensation of the gas and E_1 E_L is net heat of adsorption.

Derivation of B.E.T Equation

If at any time θ_1, θ_2 and θ_3 ….. are the fractions of the surface covered by single, double and triple complexes respectively, then the extent of adsorption is given by the volume of the gas adsorbed on the surface. Then

$$V=V_{m}(\theta_{1}+2\theta_{2}+3\theta_{3}+\ldots) \tag{6.160}$$

Where V_m is the volume of the adsorbed gas to form unimolecular layer or it is the capacity for one dense layer.

Since equilibrium exists between different phases, hence expressions for the equilibrium constants of the reactions are

Fraction of surface covered α Naked surface × Number of molecules striking per unit area

Fraction of surface covered α $(1 \quad \theta) \times P$

Fraction of surface covered α $\theta_o \times P$

So

$$\theta_{1}=K_{1}P\theta_{o}$$

$$K_{1}=\frac{\theta_{1}}{P\theta_{o}} \tag{6.161}$$

Similarly

$$K_{2}=\frac{\theta_{2}}{P\theta_{1}} \tag{6.162}$$

$$K_{3}=\frac{\theta_{3}}{P\theta_{2}} \tag{6.163}$$

Where θ_0 is the fraction of free surface at equilibrium. The difference between K_1 and K_2 is usually large because K_1 is very greater than K_2. This is due to sharp reduction in adsorbate-adsorbent interaction with increase in distance. The difference between K_2 and K_3 or K_3 and K_4 are very small, hence it is assumed that

$$K_2 = K_3 = K_L \tag{6.164}$$

Where K_L is the equilibrium constant for saturated vapour-liquid transition and is given by

$$K_L = \frac{1}{P_o} \tag{6.165}$$

Thus from equations (6.161) to (6.164), we have

$$\theta_2 = K_2P\theta_1 = K_LP\theta_1 = \left(\frac{P}{P^o}\right)\theta_1$$

$$\theta_3 = K_3P\theta_2 = K_LP\theta_2 = \left(\frac{P}{P^o}\right)\left(\frac{P}{P^o}\right)\theta_1 = \left(\frac{P}{P^o}\right)^2\theta_1$$

....

....

$$\theta_i = K_iP\theta_{i-1} = K_LP\theta_{i-1} = \left(\frac{P}{P^o}\right)^{i-1}\theta_1 \tag{6.166}$$

Using equation (6.166), equation (6.160) is modified as

$$V = V_m\left(\theta_1 + \left(\frac{P}{P^o}\right)^2\theta_1 + \left(\frac{P}{P^o}\right)^3\theta_1 + \ldots\right)$$

$$V = V_m\theta_1\left(1 + \left(\frac{P}{P^o}\right)^2 + \left(\frac{P}{P^o}\right)^3 + \ldots\right)$$

$$V = V_mK_1P\theta_o\left(1 + \left(\frac{P}{P^o}\right)^2 + \left(\frac{P}{P^o}\right)^3 + \ldots\right) \tag{6.167}$$

Using binomial theorem, for values $P \le P_o$ we have

$$\left(1 + \left(\frac{P}{P^o}\right)^2 + \left(\frac{P}{P^o}\right)^3 + \ldots\right) = \frac{1}{\left(1 - \frac{P}{P^o}\right)^2}$$

Putting this value in equation (6.167) we have

$$V = V_m\left(\frac{K_1P\theta_o}{\left(1 - \frac{P}{P^o}\right)^2}\right) \tag{6.168}$$

The total coverage of the surface

$$\theta_o + \theta_1 + \theta_2 + \theta_3 + \ldots = 1$$

Putting values of θ_1, θ_2, θ_3 .... into above equation

$$\theta_o + K_1P\theta_o + \left(\frac{P}{P^o}\right)K_1P\theta_o + \left(\frac{P}{P^o}\right)^2 K_1P\theta_o + \ldots = 1$$

$$\theta_o\left(1 + K_1P + \left(\frac{P}{P^o}\right)K_1P + \left(\frac{P}{P^o}\right)^2 K_1P + \ldots\right) = 1$$

$$\theta_o\left(1 + K_1P\left(1 + \left(\frac{P}{P^o}\right) + \left(\frac{P}{P^o}\right)^2 + \ldots\right)\right) = 1$$

As $1 + r + r^2 + \ldots. + \infty = \dfrac{1}{1-r}$, so above equation is modified as

$$\theta_o\left(1 + \frac{K_1P}{\left(1 - \frac{P}{P^o}\right)}\right) = 1 \tag{6.169}$$

$$\theta_o\left(\frac{1 - \frac{P}{P^o} + K_1P}{1 - \frac{P}{P^o}}\right) = 1$$

$$\theta_o = \left(\frac{1 - \frac{P}{P^o}}{1 - \frac{P}{P^o} + K_1P}\right) \tag{6.170}$$

Substituting the value of θ_o from equation (6.170) into (6.168)

$$V = V_m\left(\frac{K_1P\left(\dfrac{1 - \frac{P}{P^o}}{1 - \frac{P}{P^o} + K_1P}\right)}{\left(1 - \frac{P}{P^o}\right)^2}\right)$$

$$V = V_m\left(\frac{K_1P}{\left(1-\frac{P}{P^o}\right)\left(1-\frac{P}{P^o}+K_1P\right)}\right)$$

$$V = V_m\left(\frac{K_1P}{\left(1-\frac{P}{P^o}\right)\left(1+\frac{K_1PP^o-P}{P^o}\right)}\right)$$

$$V = V_m\left(\frac{K_1P}{\left(1-\frac{P}{P^o}\right)\left(1+\left(K_1P^o-1\right)\frac{P}{P^o}\right)}\right) \qquad (6.171)$$

As $\quad K_1P = (K_1P)\frac{P^o}{P^o} = \frac{K_1}{K_L}\left(\frac{P}{P^o}\right) = c\left(\frac{P}{P^o}\right)$

and $\quad K_1P^o = \frac{K_1}{K_L} = c$

Putting value of K_1P and K_1P^o into equation (6.171)

$$V = V_m\left(\frac{c\left(\frac{P}{P^o}\right)}{\left(1-\frac{P}{P^o}\right)\left(1+(c-1)\frac{P}{P^o}\right)}\right)$$

This is the B.E.T equation for adsorption. It involves vapour pressure (P), saturated vapour pressure (P^o) at the temperature of the experiment, and two constants V_m and c. This equation can be rearranged as

$$V\left(1-\frac{P}{P^o}\right) = \frac{V_mc\left(\frac{P}{P^o}\right)}{\left(1+(c-1)\frac{P}{P^o}\right)}$$

$$\frac{1}{V\left(1-\frac{P}{P^o}\right)} = \frac{1+(c-1)\frac{P}{P^o}}{V_mc\left(\frac{P}{P^o}\right)}$$

$$\frac{\frac{P}{P^o}}{V\left(1-\frac{P}{P^o}\right)} = \frac{1+(c-1)\frac{P}{P^o}}{V_mc}$$

$$\frac{\frac{P}{P^o}}{V\left(1-\frac{P}{P^o}\right)}=\frac{1}{V_m c}+\frac{(c-1)\frac{P}{P^o}}{V_m c}$$

$$\frac{\frac{P}{P^o}}{V\left(1-\frac{P}{P^o}\right)}=\frac{1}{V_m c}+\frac{(c-1)P}{V_m cP^o}$$

$$\frac{\frac{P}{P^o}}{V\left(\frac{P^o-P}{P^o}\right)}=\frac{1}{V_m c}+\frac{(c-1)P}{V_m cP^o}$$

$$\frac{P}{(P^o-P)V}=\frac{1}{V_m c}+\frac{(c-1)P}{V_m cP^o}$$

Interpretation of B.E.T Equation

1. B.E.T equation suggests that the plot of $\frac{P}{(P^o-P)V}$ versus $\frac{P}{P^o}$ should give a straight line. This has been found to be so experimentally (Fig. 6.39) which confirms the correctness (validity) of BET equation.

$$\text{Slope}=\frac{(c-1)}{V_m c}$$

$$\text{Intercept}=\frac{1}{V_m c},\ c=\frac{1}{V_m\times\text{Intercept}}$$

By adding slope and intercept, we get

$$\text{Slope}+\text{Intercept}=\frac{c-1}{V_m c}+\frac{1}{V_m c}$$

$$\text{Slope}+\text{Intercept}=\frac{c-1+1}{V_m c}$$

$$\text{Slope}+\text{Intercept}=\frac{1}{V_m}$$

From above two equations, the value of V_m and c (volume of gas to form monomolecular layer) can be calculated.

2. It is easy to see that when only unimolecular layer is formed on the surface, the BET equation would reduce to Langmuir equation.

3. The scheme of multilayered adsorption followed in BET theory can be represented as shown in Fig. 6.40.

4. BET equation is better to obey by process involving high value of $(E_1 \ E_L)$ as under such condition only the adsorbate-adsorbent interaction is predominant.

For adsorption process, the variation of equilibrium constant with temperature is given by Vont Hoff's equation

$$\Delta G = -RT \ln K$$

$$K = e^{\frac{\Delta G}{RT}}$$

So

$$K_1 = g_1 e^{\frac{E_1}{RT}}$$

$$K_L = g_L e^{\frac{E_L}{RT}}$$

Here E_1 is heat of adsorption of first layer, E_L is heat of condensation and g_1 and g_2 are various distinguishable states of adsorption.

$$c = \frac{K_1}{K_L} = \frac{g_1 e^{\frac{E_1}{RT}}}{g_L e^{\frac{E_L}{RT}}} = \frac{g_1 e^{\frac{E_1}{RT} - \frac{E_L}{RT}}}{g_L} = ge^{\left(\frac{E_1 - E_L}{RT}\right)}$$

If we ignore the energy states then

$$c = e^{\left(\frac{E_1 - E_L}{RT}\right)} = e^{\left(\frac{E_1 - E_L}{KN_A T}\right)}$$

Where K is Boltzmann's constant while N_A is Avogadro's number. $E_1 - E_2$ represents the difference between the heat of adsorption of first layer and heat of condensation. $E_1 - E_2$ is net heat of adsorption. The B.E.T equation is better obeyed by processes involving high values of $E_1 - E_2$, as under such conditions only adsorbate-adsorbent interaction is predominant.

Limitations of BET Theory

1. The assumption that adsorbate has liquid properties is not occurred.
2. When the net heat of adsorption $(E_1 - E_L)$ is low, the constant C in BET equation is small. At $C < 2$, the BET equation gives a concave isotherm.
3. BET equation holds good when p/p^o values lie between 0.05 and 0.35. This equation fails if p/p^o is below 0.05 and above 0.35.
4. Coordination number of molecules is the higher layers also add to the criticism of the BET equation in another way.
5. Low adsorbate-adsorbent energies, however the adsorbate-adsorbent interactions cannot be neglected. In the cases the isotherm (i.e. curves) are more complicated in shape.

Thus BET equation is approximate and needs modification.

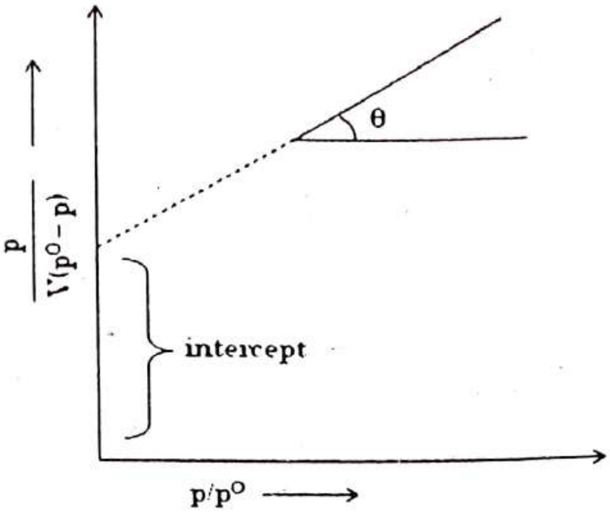


Fig. 6.39 Testing of BET equation

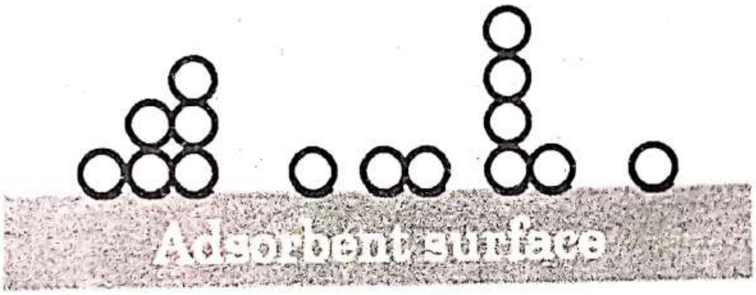


Fig. 6.40 Scheme of multi-layer adsorption

6.14 SURFACE AREA DETERMINATION OF SOLID ADSORBENTS

Generally the solid adsorbents which are used in adsorption are porous and used in powder form. So surface area of adsorbents gets increased. This enhances the magnitude of adsorption. The question of the surface area possessed by finely divided solid is not only important in adsorption, but also in contact catalysis and many other fields. BET isotherm showed that it is possible to use adsorption of gases by such materials for determination of their surface areas and thus finished a very powerful tool being widely used at present.

The porous solid adsorbents possess two types of surface areas: (A) external or outer surface area of porous particles and (B) inner surface area which is due to inner walls of capillaries and cracks in the porous particles.

The roughness factor of the catalyst is defined as

$$\text{Roughness factor} = \frac{\text{Total surface area}}{\text{Outer surface area}}$$

Hence (i) for smooth surface, roughness factor is unity and (ii) for rough surface, it is very high.

$$\text{Specific surface area} = \frac{\text{Surface area}}{\text{Mass of adsorbent}}$$

The following methods are employed to determine the surface rea of solid adsorbents.

(i) BET method

(ii) Point B method

(iii) Radioactive tracer method

(iv) Electron micrograph method

(i) BET Method

This method is extensively used for determination of surface area. The BET equation is

$$\frac{P}{(P^{o}-P)V}=\frac{1}{V_{m}c}+\frac{(c-1)P}{V_{m}cP^{o}}$$

The plot of $\frac{P}{(P^{o}-P)V}$ versus $\frac{P}{P^{o}}$ should give a straight line. This has been found to be so experimentally (Fig. 6.39) which confirms the correctness (validity) of BET equation.

$$\text{Slope}=\frac{(c-1)}{V_{m}c}$$

$$\text{Intercept}=\frac{1}{V_{m}c}$$

By adding slope and intercept, we get

$$\text{Slope}+\text{Intercept}=\frac{1}{V_{m}}$$

$$V_{m}=\frac{1}{\text{Slope}+\text{Intercept}}$$

By calculating value of slope and intercept from graph and putting in above equation, V_m is calculated.

As

22400 mL of gas at NTP contains = N_A molecules

1 mL of gas at NTP contains = $N_A/22400$ molecules

V_m mL of gas at NTP contains = $V_mN_A/22400$ molecules

If A is the area of cross-section of each adsorbent molecule, i.e. the area of surface covered by each molecule and m is the mass of adsorbent, then surface area of solid adsorbent will be

$$\text{Surface area of solid adsorbent}=\frac{N_{A}V_{m}A}{22400}$$

Specific surface area = Surface area per gram of adsorbent

$$\text{Specific surface area} = \frac{N_A V_m A}{22400 \times m}$$

In BET method, nitrogen gas is commonly used at its boiling point (-195.8 °C). At this temperature 16.2×10^{-20} m² is the area of nitrogen molecule.

Table 6.1 Estimates surface area of clean Nickel films from the physical adsorption of various gases

Gas	Area per molecule ($\times10^{-20}$) m²	Amount adsorbed to give monolayer on 1 g Ni film	Surface area of 1 g Ni film (m²)
Kr	14.6	6.15×10^{19}	9.0
Kr	14.6	5.85×10^{19}	8.6
CH_4	15.7	5.40×10^{19}	8.5
n- C_4H_{10}	24.5	3.48×10^{19}	8.5

Table 6.2 Volumes of adsorbed nitrogen to form a monolayer and surface area of a number of catalysts

Material	Monolayer volume (liter at STP g^{-1})	Surface area (m²/g)
Fused Cu catalyst	0.09×10^{-3}	0.39
Fe, K_2O catalyst 930	0.14	0.61
Fe, Al_2O_3, K_2O catalyst 931	0.81	3.5
Cr_2O_3 gel	53.3	230
Silica gel	116.2	500

(ii) Point B Method

In this method relative pressure P/P^o is plotted against volume of gas adsorbed. The curve is shown in Fig. 6.41 is obtained.

Point B is the first inflexion point in the curve and it corresponds to the condition when unimolecular layer is formed.

If V_B is the volume of the gas corresponding to point B, reduced to standard conditions (P_o = 1 atm and T_o = 273 K)

Then $P_o V_B = nRT_o$

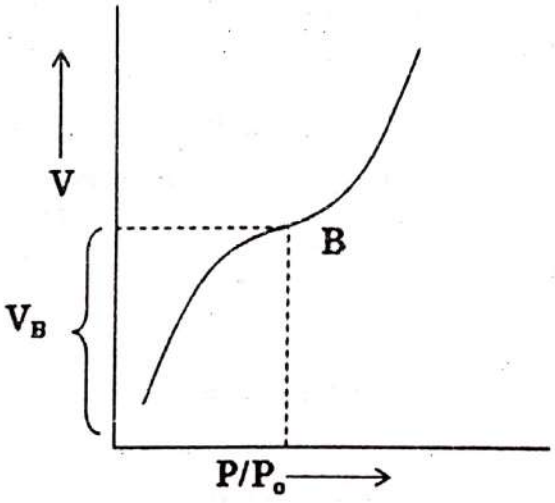


Fig. 6.41 Plot of V versus P/P_o

$$n = \frac{P_o V_B}{RT_o}$$

Where n is the number of moles.

Number of molecules adsorbed = n N_A

$$\text{Number of molecules adsorbed} = \frac{P_o V_B N_A}{RT_o}$$

If A is area of cross-section of each adsorbed molecules, then total surface area is

$$\text{Total surface area} = \frac{AN_A P_o V_B}{RT_o}$$

$$\text{Specific surface area} = \frac{AN_A P_o V_B}{mRT_o}$$

This method cannot be applied to all types of solid adsorbents and gas adsorbates. Generally nitrogen is used in this method. The value of A for nitrogen is measured by using following formula

$$A = \left(\frac{M}{\rho N_A}\right)^{2/3}$$

Where ρ is density of nitrogen and M is its molecular weight.

QUESTIONS

Q.1. The rate of catalytic reaction of two gases on solid surface is

$$\text{Rate} = \frac{aP_A bP_B}{(1 + aP_A + bP_B)^2}$$

(i) Discuss the effect of pressure of gas A on rate of reaction at constant P_B under various conditions.

(ii) Prove that the rate of reaction is maximum at $P_A = (1+bP_B)/a$

Q.2. Langmuir adsorption isotherm for single system is

$$\theta = \frac{bP}{1 + bP}$$

(i) Rearrange above expression in the form of equation of straight line. Draw a plot according to this equation.

(ii) Explain the effect of equilibrium pressure on fractional surface coverage.

(iii) Derive kinetic rate equation for catalytic decomposition of a gas on metal surface when reactant gas is weakly adsorbed.

Q.3. Derive the relation for rate of decomposition of ammonia using Tempkin's Isotherm.

Q.4. The rate of enzyme catalyzed reaction is

$$\upsilon = \frac{k_2[E]_0[S]}{k_M + [S]}$$

(i) Explain the parameters present in this relation.

(ii) Give plot of υ as a function of [S].

(iii) Discuss the effect of substrate concentration on rate of reaction.

(iv) Define k_M in term of substrate concentration and give its units.

(v) How can you evaluate k_2 and k_M from above expression.

(vi) Give condition for maximum rate of enzyme catalyzed reaction.

(vii) How can you find the value of k_M graphically.

Q.5. The rate of catalytic reaction of two gases on solid surface is

$$\text{Rate} = \frac{aP_A bP_B}{(1 + aP_A + bP_B)^2}$$

(i) Derive the relation for P_A in term of a and b at which rate of reaction is maximum.

(ii) Prove that the %age rate fall is only 11 % when P_A is twice the optimum value.

(iii) Discuss the effect of P_A and P_B on rate of reaction on following conditions.

(a) When A and B both gases are weakly adsorbed.

(b) When gas A is strongly adsorbed.

Q.6. Differentiate the followings

(i) Langmuir Hinshellwood mechanism and Eiley Rideal mechanism

(ii) Adsorption and desorption

(iii) Physical adsorption and chemical adsorption

Q.7. Calculate the pressure of a gas using Langmuir adsorption isotherm at which fractional surface coverage is

(i) 0.2 (ii) 0.8

Q.8. The hydrolysis of fumarate is carried out in the presence of enzyme, the fumarase as

$$\text{Fumarate} + H_2O \xrightarrow{\text{Fumarase}} \text{L-Malate}$$

The value of k_2 for this enzyme is $3\times10^{3}\,s^{-1}$ and k_M is $4\times10^{-5}\,M$. Calculate the rate of fumarate conversion if the initial concentration of fumarate is $1\times10^{-5}\,M$ and fumarate concentration is $4\times10^{-4}\,M$.

Q.9. At 300 K, when the pressure of gas is 40 kPa the sample adsorbs 0.72 mg of CO. At same temperature, the mass of gas adsorbed is 0.24 mg at 8 kPa. By using Langmuir adsorption isotherm find the fractional surface coverage of surface at two pressures. ($\theta_A = 0.75$, $\theta_B = 0.375$)

Q.10. Adsorption of a gas on solid obeys Langmuir adsorption isotherm. At 6.71 kPa and 20°C gas adsorbs 2.56 mg. The enthalpy change is 10.9 J when 1 mmol of the adsorbed gas is desorbed. What is the pressure for adsorption of same gas at 40°C. ($P_2 = 14.5$ kPa)

Q.11. Explain the kinetics of reaction of two gases on solid surface.

Q.12. Discuss heterogeneous kinetics of single system reactions. Explain the phenomenon of retardation by reactants and products.

Q.13. Discuss the kinetics of heterogeneous reactions. Explain retardation of rate of reactions by products and reactants.

Q.14. What do you understand about heterogeneous kinetics? Explain the kinetics of a single reacting gas on solid surface.

REFERENCES

1. Logan, S.R. 1996. Fundamentals of Chemical Kinetics, Longman Group Ltd.
2. Bond, G. C. 1987. Heterogeneous Catalysis: Principles and Applications 2nd Edition, Oxford, Clarendon Press.
3. Gutfreund, H. 1972. Enzymes: Physical Principles, Wiley, New York.
4. Benson, S. W. 1976. Thermochemical Kinetics, Wiley, New York.
5. Moore, W.J. 1995. Physical Chemistry, Prentice-Hall, Englewood Cliffs, New Jersey.
6. Kundu, N and Jain, S. K. 2001. Physical Chemistry, Chand and Company Ltd. New Delhi.
7. Barrow, G.M. 1997. Physical Chemistry, GcGraw Hill, Tokyo.
8. Atkins, P.W. 2005. Physical Chemistry, Freeman and Company, New York.
9. Satterfield, C. N. 1980, Heterogeneous Catalysis in Practice, McGraw-Hill Book Co., New York.
10. Hammes, G. G. 1978. Principles of Chemical Kinetics, Academic Press, New York.

Chapter 7

NUCLEAR AND RADIO CHEMISTRY

7.1 INTRODUCTION

Nuclear chemistry is a branch of science which deals with the composition, properties and reactions of atomic nuclei. It is concerned with the structure of nuclei, their stability and conversion into other nuclei. It deals with the study of changes in or transformations of the atomic nuclei and includes spontaneous and induced radioactivity, the fission of nuclei and their fusion, the properties and behavior of reaction products, their separation and analysis. Chemical reactions or changes involve the transfer or sharing of electrons. However, the usual properties of the nuclei, mass, atomic number and nuclear structure – bear no direct relation to chemical reactions. In other words, the chemical properties of the elements depend upon the electronic arrangements of the atoms and the behavior of the electrons in the valence shell. Nothing happens to the nuclei of the atoms during chemical reactions, e.g.

$$AgNO_3 + NaCl \longrightarrow AgCl\downarrow + NaNO_3$$

$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2\uparrow$$

Consequently there can be no direct relationship between the chemical and nuclear properties of atoms. On the other hand, a wide variety of phenomenon are of interests to chemists either because certain nuclear properties provide new chemical tools or because differences in nuclei actually produce subtleties of chemical behavior. Thus, nuclear chemistry includes any of the relationship between atomic and nuclear structure of importance to a chemist.

During the past eighty years much work has been done in the field of science dealing with the nature and reactions of fundamental particles and atomic nuclei by both physicists and chemists. Nuclear chemistry has become a very important and fascinating branch of science due to the tremendous amount of energy liberated during nuclear reactions which led to the discovery of atomic and hydrogen bombs etc. The controlled release of nuclear energy promises to lead us into a new era, in which an unlimited source of energy is available to mankind. It is rightly said that we are now living in the nuclear age and the future of humanity is at the mercy of nuclear chemists and physicists. They can annihilate (destroy completely) the whole world within a few minutes. They are the hope of human happiness and prosperity as well.

In general, the nuclear chemist is concerned with these properties involving similarities and differences among the isotopes of a given element. In addition to stable isotopes, the nuclear chemist studies unstable or radioactive isotopes by the applications of various techniques of radiochemistry and radiation chemistry. We often use the term "*Radiochemistry*" to describe the work with radioactive species whereas "*Radiation Chemistry*" is now limited to the chemical effects brought about by radiation interactions with a system. In developing the basic concepts of nuclear chemistry we will be concerned with nuclear structure, nature of radiation and their measurement. identification of various isotopes, laws of radioactive growth and decay and applications of radiation in daily life. All of this information serves as the starting point for any-one entering in the field of nuclear chemistry, either as a specialist or as a person wishing to add its special techniques to his training. The basic concepts of nuclear chemistry stem more from physics than from chemistry but we can say that chemistry is the bridge across which we must walk to put the atom to work.

7.2 THE ATOM

An atom is the smallest possible particle of an element that can take part in a chemical reaction. The present concept of the atom, gained after innumerable scientific investigations over many decades is that it is composite, hence divisible and synthesizable with effort. It is now universally accepted that the atom consists of two distinct regions: the tiny central core called the *nucleus* having a radius of the order of ~10^{-15} m or 10^{-13} cm, and the relatively extensive surrounding space referred to as the *outer space* which has the radius of the order of ~10^{-10} m or 10^{-8} cm. The millions of the forms of matter found in the universe are a result of the endless ways in which the atoms combine.

Our present concept of the atom includes the notion that atom consists of a very small, dense and positively charged nucleus surrounded by a number of negativity charged particles, the electrons occupying certain positions, following certain paths of motion. The nucleus consists of protons and neutrons, and these two particles are usually known as *nucleons*. In other wards, these fundamental particles protons, neutrons and electrons-constitute an atom. Of these, protons and neutrons are present in the nucleus and the electrons exist in different spherical shells outside the nucleus. The chemical behaviour of the elements is determined by the distribution of the electrons in the atom with particular significance being given to the number and arrangements of the outer-most or valence electrons. The protons and neutrons contained in the nucleus contribute to the nuclear properties of the atom.

7.3 THE ATOMIC NUCLEUS

The nucleus is the central core of an atom. What exactly the atomic nuclei contain is still uncertain. It was believed that the nuclei contain neutrons and protons, which are commonly known as *nucleons*. But after the discovery of various sub nuclear particles, the nuclear picture seems to be complicated. Nevertheless, there are several reasons which indicate that the nucleus is not necessarily be a mixture of all the sub-nuclear particles. All these particles do not exist as components of the nucleus. Since these particles have been detected in the products of various nuclear reactions, it is now generally believed that the nucleus is composed of neutrons and protons.

The composition and structure of the atomic nucleus remained a riddle for a long time. The proposal in 1898 by J.J. Thomson, that the atom consists of a number of negative particles moving around a sphere of positive charge was the basis for further understanding of the nucleus.

Rutherford's model of atom:

Rutherford (1913), based on his experiment on the interaction of alpha particles with atomic nuclei proposed the following regarding the atom:

(i) An atom consists of a positively charged central nucleus.

(ii) The atomic nucleus is very small compared with the size of the atom as a whole.

(iii) Electrons are distributed around the nucleus, whose number equals the nuclear charge (positive).

(iv) Most of the mass of the atom is contributed by the nucleus.

(v) There are empty spaces in the atom, the spaces exist between the nucleus and the electrons.

These descriptions of the atom were based on his alpha particle scattering experiment. Alpha particles from a radioactive source were made to hit a thin metal foil (Fig. 7.1). Then the changes in their paths were traced with a ZnS screen on which the particles produced scintillations.

Some of the alpha particles first passed through the metal foil. This indicates that the atom has empty space. At the same time some of the alpha particles passed through the metal foil, but with large deflections. This proves the existence of electric fields inside the atom. The positive alpha particles experience repulsion with the positive nucleus and therefore get deflected. The other alpha particles are deflected backwards. These particles presumably hit the nucleus head-on, and are turned back. This experiment led to significant understanding of the nature of the atomic nucleus.

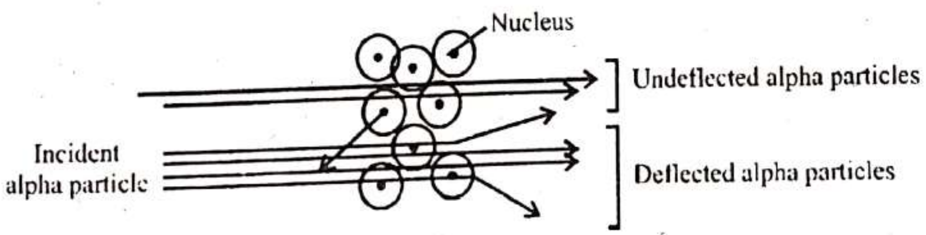


Fig. 7.1. Rutherford's alpha particle scattering experiment.

Following are some important properties of the nucleus.

(i) Nucleus of an atom consists of fundamental particles protons and neutrons.

(ii) The forces that bind the electrons to the neutrons are electrical or coulombic in nature.

(iii) The size of the nucleus is measured in Fermi units

(1 Fermi = 10^{-13} cm or 10^{-15} m)

(iv) The diameter of an atom is of the order of 10^{-8} cm or 10^{-10} m, while that of nucleus is 10^{-13} to 10^{-12} cm. The size of the nucleus is 1/1000th of the size of an atom.

(v) The radius of the nucleus is around 5×10^{-12} cm and that of electron is 2.8×10^{-13} cm

(vi) The volume of the nucleus is about 10^{-36} cm^3 and that of atom is $10^{-24} cm^3$. The volume of nucleus is thus 10^{-12} times that of an atom.

(vii) The density of the nucleus is enormous and is of the order of 10^{14} g/cm^3

(viii) Density of the nucleus is constant for any nuclide.

7.4 COMPOSITION OF THE NUCLEUS

The alpha-particle scattering experiments of Rutherford and his school not only confirmed the nuclear model and led to the determination of nuclear charges, but also gave some information of sizes of the nuclei. Since the nucleus contains nearly the entire mass of an atom, it follows that nuclei are very much denser than ordinary matter, the density of nuclear matter is in the neighborhood of 10^{14} g/cm^3.

Any theory of the structure of the nucleus must account for the mass as well as for the charge. The nucleus contains almost the entire mass (~ 99.95%) of the atom, and the atoms of each element have nuclei of characteristic charge, i.e., a positive charge equivalent to the number of electrons surrounding the nucleus. In order to explain the structure of nucleus, various hypotheses have been proposed. These hypotheses may be named according to the elementary particles regarded on the constituents of nucleus.

(i) Electron-Proton Model of the Nucleus: Prior to the discovery of neutron in 1932, it was generally believed that a nucleus of an atom was composed of protons and electrons. Accordingly, this is named as proton-electron hypothesis or model. According to this hypothesis, it was considered to assume that the nucleus, whose atomic weight is very nearly an integer A, contained A protons (the mass of protons is approximately unity on the ordinary atomic weight scale). In such a case, the charge of the nucleus would be equal to A, nearly the same as the atomic weight and not equal to atomic number Z, which is half or less, of atomic weight. Therefore, it was assumed that in addition to the protons, the nucleus contained (A-Z) electrons to make the net positive charge, i.e., A-(A-Z) = Z equal to the atomic number of the element. The number of electrons was considered to contribute a negligible amount to the total mass. It was thus possible to consider the atom as consisting of a nucleus of A protons and A-Z electrons surrounded by Z extra nuclear electrons.

This proton-electron hypothesis posed a number of difficulties. In order to be contained in a nucleus an electron would have to have a de-Broglie wavelength no larger than nuclear dimmsions (~ 10^{-12} cm). The kinetic energy corresponding to such a de-Broglie wavelength is more than an order of the magnitude larger than the energy of $\beta-$particles emitted by nuclei, which cast doubts on the idea of free electrons as constituents in nuclei. Other difficulties stemmed from consideration of angular momentum conservation and statistics in nuclei with odd Z and even A, such as N^{14}.

(ii) Proton-neutron Model of the Nucleus:

In 1932, J. Chadwick discovered neutron which is a neutral particle of zero charge and of mass approximately equal to that of proton. (Actually it is slightly greater than that of proton). Since electron-proton model was not able to explain several nuclear properties, it was quickly discarded after the discovery of neutron. It is now believed that the nucleus is made up of protons and neutrons. According to this picture, the number of protons in a nucleus equals to atomic number Z, and the total number of neutrons and protons (collectively called *nucleons*) equals its mass number A. Therefore, the neutron number N equals A-Z. Thus nucleus of N^{14} is thought to contain 7 protons and 7 neutrons. The difference N-Z (or A-2Z) between the number of neutrons and protons in a nucleus in referred to as its *neutron excess* or *isotopic number*.

This theory contradicts the proton-electron hypothesis of nuclear composition. Since the size of the proton and neutron is much smaller than the size of the electron, the size of the nucleus will be even smaller than the size of the electron. This suggests that electron cannot exist in the atomic nuclei. Finally, since the mass of the neutron is very close to that of proton, the argument favouring the existence of the protons in the nucleus is also valid for the neutrons. The proton-neutron hypothesis thus explains nearly all the difficulties raised against the proton-electron hypothesis. This hypothesis is now accepted hypothesis of nucleus composition.

7.5 PROPERTIES OF THE NUCLEUS

Nuclear Energy Levels:

Like atomic electrons, the nucleus also exists in several energy states. The difference in the energy gap between nuclear levels is much larger as compared to electronic levels. In general, the energy separation of nuclear levels is of the order of a million electron volt (or 10^6 eV). If $E_2 - E_1$ is set equal to 1MeV, the λ of the radiation corresponding to such a transition would be about 1.2×10^{-12} cm. Such a λ corresponds to short X-rays or long gamma rays. Thus gamma rays are emitted due to transition of nucleus from higher (excited) energy level to lower level.

Nuclear Spin:

The neutrons and protons which constitute the nucleus are not stationary particles. Like our earth, they also have spin and orbital motions. The spin and orbital angular momenta of the individual neutrons and protons in a nucleus combine to give a resultant angular momentum generally referred to as the "spin" of the nucleus. The nucleus spin is usually denoted by I. The spins of the nuclei with odd mass numbers are.

$$I = 1/2, 3/2, 5/2, 7/2 \text{ etc}$$

Whereas the spins of nuclei with even mass numbers an

$$I = 0, 1, 2, 3, 4, \text{etc}$$

The spins of nuclei with even mass in their ground state is usually 0 or 1.

Nuclear Magnetic Moment:

Motion of the electrical charge is called current. A wire carrying the current deflects the magnetic needle, if it is brought near the wire carrying current. This means that the motion of the charge generates a magnetic field. An electron (or proton) is a rotating charged particle. Therefore it behaves like a small magnetic dipole. Its magnetic moment is given by

$$\mu = \frac{eh}{4\pi mc} \tag{7.1}$$

and is a measure of the intrinsic magnitude of the generated dipole. e is the electronic charge, m is the rest mass of an electron, c is the velocity of light. The magnetic moment of an electron is called one Bohr magneton. The magnetic moment of proton can also be calculated by the above equation by replacing the mass of $\bar{e}$ with that of proton. Since proton is 1836 times heavier than electron, its magnetic moment is 1836 times less than that of $\bar{e}$. The magnetic moment of a proton is called one nuclear magneton. The magnetic moments of nuclei are of the order of one or a few nuclear magnetons. The magnetic properties of an electron are utilized in the working of ESR and that of nucleus in the working of NMR, spectrometers.

7.6 THE FUNDAMENTAL PARTICLES

As discussed in the preceding section, an atom consists of protons, neutrons and electrons. Except the hydrogen nucleus, all other atomic nuclei contain protons and neutrons. After the discovery of radioactivity, a number of transformations were observed which are associated with changes in the nucleus of atom. Such transformations are the nuclear reactions, some take place spontaneously, while others are brought about artificially by bombarding the nuclei with different energized particles.

The atom consists of protons, neutrons and electrons. These particles are called fundamental particles or subatomic particles. Several other particles such as positron, neutrino, mesons etc are also called the fundamental particles. A fundamental particle is either a constituent particle of a nucleus or one that is produced from a nucleus. The fundamental particles can be classified by different ways, based on their stability or mass.

The fundamental particles may be classified as stable and unstable particles. The protons and electrons are stable particles, the neutrons and position are some of the unstable particles.

Based on mass, the particles are grouped into mass particles and energy (massless) particles. The protons and electrons are some of the mass particles. The gamma ray photon, graviton and neutrino are massless particles. Besides the gamma-photon, 32 fundamental particles have been postulated and experimental verification of the identity of all but a few has been achieved.

The important properties by which these particles are defined are their charge, mass and spin. A brief description of some of these particles is given below:

(i) The Electron

The electron was the first to be recognized as a sub-atomic particle. Jean Perrin in 1885 suggested its negative charactor. In 1897, J.J. Thomson proved that electrons are a constituent of all types of matter. The electrical charge on electron is 4.8×10^{-10} e.s.u. and this is chosen as the standard unit of electrical charge. It is very tiny particle with a radius of 2.82×10^{-15} m. It has a spin of ½. It is a stable particle. It has a mass of 0.00055 atomic mass unit (9.108×10^{-28} g).

(ii) The Proton

All atomic nuclei contain protons. The electrical charge of a proton is equal to that of an electron in magnitude but of opposite sign. Its spin is ½. It is a stable particle. Rutherford was the first to produce the proton through an artificial nuclear reaction.

$${}_7N^{14} + {}_2He^4 \longrightarrow {}_8O^{17} + {}_1H^1$$

(iii) The Neutron

James Chadwick discovered the neutron by bombarding ${}_4Be^9$ with alpha particles.

$${}_4Be^9 + {}_2He^4 \longrightarrow {}_6C^{12} + {}_0n^1$$

All the nuclei except hydrogen nucleus, contain neutrons. The neutron is an unstable particles outside the nucleus. It decays outside the nucleus, into a proton, an electron and antineutrino.

$${}_0n^1 \longrightarrow {}_1H^1 + \bar{e} + \bar{v}$$

Direct measurements of the neutron spin have shown that it is ½ and not 0 or 1 as would be the case if it were composed of two particles. The present accepted neutron mass is 1.008665 a.m.u.

(iv) The Positron

It is the antiparticle for the electron. C-D. Anderson (1932) proved its existence in the cosmic rays. Its mass is same as that of electron, but its charge is unity and positive. It is a stable particle but on interaction with an electron it is destroyed into energy, two photons are produced.

$$\beta^+ + \beta^- \longrightarrow 2h\upsilon$$

This process is called annihilation interaction.

(v) The Neutrino and Antineutrino

The emission of a neutrino was postulated by Pauli (1931) during a proton decay.

$$P \longrightarrow n + \beta^+ + \upsilon$$

Similarly, the emission of an antineutrino in a beta decay was postulated by him.

$$_0n^1 \longrightarrow P + \beta^- + \upsilon^-$$

The emission of these particles is a necessity for conservation of energy and angular momentum in beta-decays. The neutrino and the antineutrino are identical in all aspects but with opposite spins. They have very low mass, 0.05 fraction of the mass of an electron. They do not have any charge and are stable particles. Neutrino is a component of cosmic rays.

(vi) Mesons

In an attempt to explain nuclear forces, Yukawa in 1934 postulated the existence of yet another particle with a mass intermediate between that of the electron and that of proton. In 1937 experimental evidence from cosmic ray studies was obtained by Anderson for the existence of both positive and negative particles with a mass 207 times that of electron. These are the μ mesons or 'muons' and the problem appeared solved. The properties of some of the fundamental particles are summarized in Table 7.1.

Table 7.1. Fundamental Particles-Summery

Particle	Symbol	Charge	Mass (amu)	Spin
Electron	β^-, e^-, e	-1	1	½
Positron	β^+, e^+	+1	1	½
Proton	P	+1	1836.1	½
Neutron	n	0	1836.6	½
Neutrino	υ	0	0	½
Antineutrino	$\bar{\upsilon}$	0	0	½
μ Mesons	μ ±	±	0.1152	0
Photon	γ	0	0	1 or ½
Graviton	G	0	0	½
Antiproton	$\bar{P}$	-	1.00758	½
V-particle	V	+/-	1.2014	?

7.7 NUCLEAR STABILITY

The nuclides may be classified as (a) stable and (b) unstable or radioactive. Stable nuclides are those which are permanent and their proton and neutron contents remain unchanged for ever, no matter how the electrons in the outer sphere may change in location or even in number. The nucleus of stable nuclides can be changed only under sever conditions, by bombardment of external radiation or particles of very high energy (~ 1.10 MeV or higher) or by neutron capture. Just 274 naturally occurring nuclides are considered stable. (A nuclide is considered stable if it remains unchanged up to 10^{21} years or more. $_{52}Te^{130}$ has a decay period of 10^{21} years.

On the other hand the unstable or radioactive nuclides are intrinsically unstable and undergo spontaneous change with time forming new nuclides by one or the other way by rearranging or losing of their protons and neutrons. Above 2000 nuclides including man made are known to be unstable or radioactive.

The question naturally arises why some nuclides are stable while the others are unstable (or radioactive): in other words what are the factors leading to nuclear stability? A study of the characteristics of a large number of stable and radioactive nuclides shows the following to be some of the important factors involved.

1. Even-odd Rule

It is also known as even-odd nature of protons and neutrons. Most naturally occurring nuclides have even numbers of protons and even numbers of neutrons. 165 nuclides fall into this category. Nuclides with odd numbers of both are least common (only five) and those with odd-even combinations are intermediate in abundance. Following table gives a summary of the stable nuclei along with the even-odd numbers of protons and neutrons in them.

Table 7.2. Frequency distribution of stable nuclides.

Z	N	A(Z+N)	No. of nuclides (stable)	Examples
Even	Even	Even	165	$_2He^4$ $_{12}Mg^{24}$ $_{82}Pb^{208}$
Even	Odd	Odd	55	$_8O^{17}$ $_{12}Mg^{25}$ $_{26}Fe^{57}$
Odd	Even	Odd	50	$_3Li^7$ $_9F^{19}$ $_{29}Cu^{68}$
Odd	Odd	Even	5	$_1H^2$ $_3Li^6$ $_5B^{10}$ $_7N^{14}$ $_{73}Ta^{180}$

A survey of this table brings to light some interesting points, of the stable nuclei, the greatest number have an even number of both P and N. and the least number have an odd number of P and N. This means that even-even nuclei are most stable and odd-odd nuclei are the least stable. This is well brought out by the composition of the earth's crust about 85% of which consists of even-Z, even-N nuclides as, (with % abundance in parenthesis) $_8O^{16}(48)$, $_{14}Si^{28}(26)$, $Fe^{56}(5)$ $_{20}Ca^{40}(3.5)$, $_{12}Mg^{24}(2)$ and about 13% of odd-Z, even-N nuclides as $_{13}Al^{27}(8.5)$, $_{11}Na^{23}(2.8)$ and $_{19}K^{39}(2.5)$.

2. Magic Numbers

It has been noted that a nucleus is more stable if its neutrons and protons numbers are 2, 8, 20, 28, 50, 82 and 126. These numbers are called magic numbers. The nucleus is most stable if its neutron and proton numbers both are magic numbers.

e.g. $_2He^4$, $_8O^{16}$, $_{20}Ca^{40}$, $_{38}Sr^{88}$ and $_{82}Pb^{208}$ etc.

Helium nucleus with two neutrons and two protons is exceptionally stable.

3. The Neutron to Proton Ratio (N/Z):

In addition to the above factors, the ratio of N/Z also determines the nuclear stability. Except in the case of ordinary hydrogen $\left({}_1H^1\right)$, all other nuclides contain both neutrons and protons. A look at the stable nuclides shows that the ratio N/Z in them is ≥ 1. The ratio is ≈ 1 in all the light stable nuclides up to $_{20}Ca^{40}$ and this after the ratio is > 1 for heavy nuclei as may be seen from Segre chart (graph between Z and N values)

Table 7.3 N/Z ratio in some stable nuclides

X^A	$_1H^2$	$_{10}Ne^{20}$	$_{20}Ca^{40}$	$_{30}Zn^{64}$	$_{40}Zr^{90}$	$_{50}Sn^{120}$	$_{60}Nd^{150}$
Z	1	10	20	30	40	50	60
N	1	10	20	34	50	70	90
N/Z	1.00	1.00	1.00	1.15	1.25	1.40	1.50

Following figure-shows a plot of the number of neutrons (N) versus number of protons (Z) for the stable nuclides.

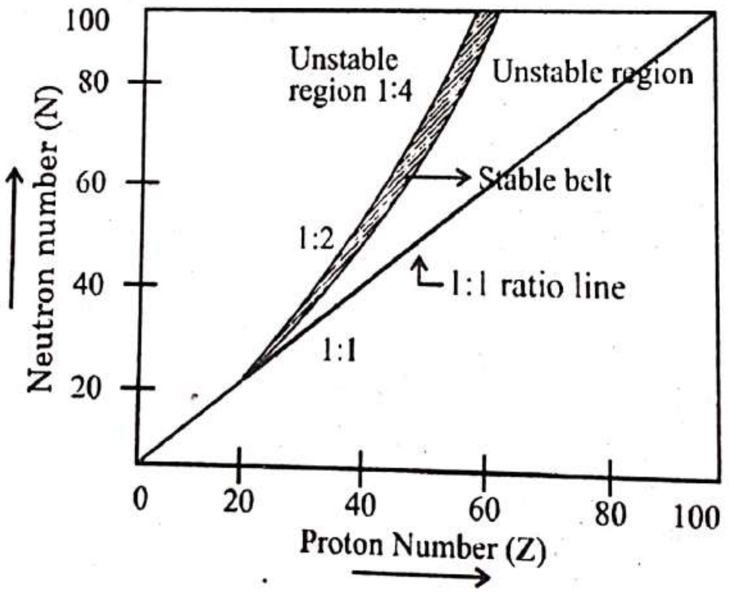


Fig. 7.1. Nuclear stability graph.

As the atomic number increases, the neutron to proton ratio of the stable nuclei increases. The stable nuclei are located in an area of the graph known as the band of stability. Since a large no. of elements have several stable isotopes, the curve is in the nature of a strip or zone which widens out at higher Z values. All stable nuclei fall within this zone. Any nucleus lying outside this zone of stability will be unstable. The nuclei above the stability zone have excess of neutrons while those lying below have more protons. Such nuclei would be unstable and can attain stability by radioactive changes in the nucleus so that N/Z ratio falls within the zone of stability.

Consider the nuclide with Z = 11 (sodium) the only stable nuclide is $_{11}\text{Na}^{23}$. Replacing a proton by a neutron results in $_{10}\text{Ne}^{23}$ which is radioactive (β^-). Similarly replacing a neutron by proton results in $_{12}\text{Mg}^{23}$ which is also radioactive (β^+). Again keeping Z constant, the removal of a neutron from or its addition to $_{11}\text{Na}^{23}$ results respectively in β^+ active $_{11}\text{Na}^{22}$ or β^- active $_{11}\text{Na}^{24}$

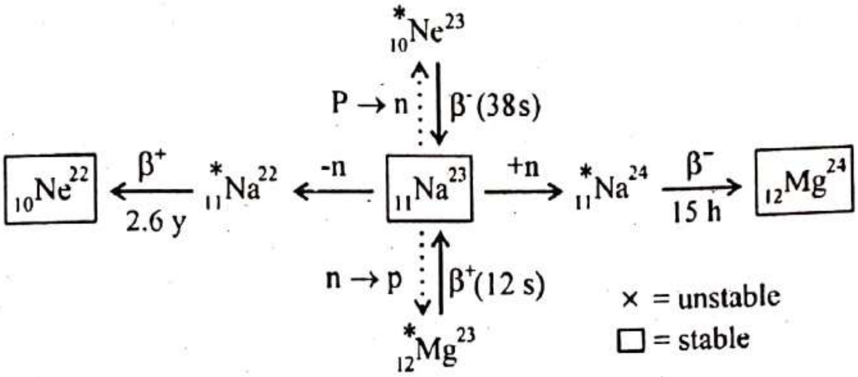


Fig. 7.3. Figure illustrating the effect of addition or removal of fundamental particles from the nuclide $(_{11}\text{Na}^{23})$

7.8 NUCLEAR TERMS

- Following are some of the commonly used nuclear terms:

(i) **Atomic number:** The number of protons in the nucleus is called the atomic number. It is represented by Z.

(ii) **Mass number:** The sum of the number of neutrons and protons in the nucleus is called mass number, A.

$$A = Z + N$$

(iii) **Neutron number:** The number of neutrons in the nucleus is called neutron number, N.

(iv) **Nucleons:** Particles comprising the nucleus are called nucleons. The nucleus contains protons and neutrons as its major components of mass. A proton carries a positive elementary charge and a neutron has no charge. Either proton or neutron is called nucleon.

(v) **Nuclides:** The terms nuclide is used to signify any one of the known species of atoms characterized by the constitution of its nucleus, in particular by the no. of protons and neutrons, in its nucleus

or

Any species of atom with a definite number of protons and neutrons is called a nuclide.

or

"Nuclides" refer to different atomic forms of all elements in contrast to "isotopes" which refer only to different atomic forms of a single element.

(vi) **Nuclide Symbol:** The composition of a nucleus is indicated by its nuclide symbol. It consists of the symbol for element (E), with the atomic number (Z) written as the subscript at the lower left and the mass number (A) as the superscript at the upper left/right $^{A}_{Z}E_{(U.K)}$ or $_{Z}E^{A}$ (U.S.A)

e.g. $^{4}_{2}He$, $^{14}_{7}N$, $^{235}_{92}U$ or $_{2}He^{4}$, $_{7}N^{14}$, $_{92}U^{235}$

The atomic number is often omitted, because it is uniquely determined by the chemical symbol. $_{7}N^{14}$, $_{7}N^{15}$ etc.

The chemical behaviour of an atom is related to number of protons/no. of electrons.

(vii) **Isotopes:** Isotopes are the atomic species (nuclides) of same atomic number Z, that is belonging to the same element, but having different mass number A (or having different neutron number N). In the nuclei of different isotopes of a given element the same no. of protons is combined with different number of neutrons. For example $_{6}C^{12}$, $_{6}C^{13}$ and $_{6}C^{14}$ are isotopes of carbon, because they contain the same number of protons (six) in their nuclei. Similarly $_{1}H^{1}$, $_{1}H^{2}$ and $_{1}H^{3}$ are isotopes of hydrogen. The word isotope has been used also in a broader sense to signify any particular nuclear species characterized by it's A and Z values.

(viii) **Isobars:** Atomic species (nuclides) having the same mass number (A) but different atomic numbers (Z) and N-values. A few examples of the isobars are $_{32}Ge^{76}$ and $_{34}Se^{76}$

$_{52}Te^{130}$, $_{54}Xe^{130}$ and $_{56}Ba^{130}$

$_{80}Hg^{204}$ and $_{82}Pb^{204}$

(ix) **Isotones:** Atomic species having the same number of neutrons but different mass number and atomic number are called isotones

e.g. $_{1}H^{3}$ and $_{2}He^{4}$ (2 neutrons each)

$_{14}Si^{30}$, $_{15}P^{31}$ and $_{16}S^{32}$ (16 neutrons each)

$_{6}C^{14}$, $_{7}N^{15}$, $_{8}O^{16}$

(x) **Nuclear isomers:** Atomic species having the same atomic number and the same mass number but differing in their energy contents or radioactive properties are called nuclear isomers. That is, nuclear isomers are the different energy states of the same nucleus, each having a measurable life time (except the ground state which may be stable). The isomers as denoted as $_{Z}X^{A}$ and $_{Z}X^{Am}$. (m = metastable)

For example three radioactive, species of half lives 60 days, 1.3 min and 21 min. have assigned to Sb^{124}

^{124}Sb (60 days) $^{124m1}Sb$ (1.3 min) and $^{124m2}Sb$ (21 min)

Example 7.1.

Determine the number of protons, neutrons and electrons in a $^{210}_{82}\mathrm{Pb}^{2+}$ ion.[7.1]

Solution.

The atomic number of lead is 82, which means this ion contains 82 protons. Since it has a charge of +2, this ion must contain 80 electrons. Because neutrons and protons both have a mass of about 1 amu, the difference between the mass number (210) and the atomic number (82) is equal to the number of neutrons in the nucleus of atom. This ion therefore contains 128 neutrons.

Example 7.2. Classify the following sets of nuclides as examples of isotopes, isobars or Isotones.

(i) $^{12}_{6}\mathrm{C}$, $^{13}_{6}\mathrm{C}$, $^{14}_{6}\mathrm{C}$

(ii) $^{40}_{18}\mathrm{Ar}$, $^{40}_{19}\mathrm{K}$, $^{40}_{20}\mathrm{Ca}$

(iii) $^{14}_{6}\mathrm{C}$, $^{14}_{7}\mathrm{N}$, $^{16}_{8}\mathrm{O}$

Solution:

(i) Isotopes, because they all contain six protons.

(ii) Isobars, because they have same mass.

(iii) Isotones, because they have same number of neutrons.

7.9 NUCLEAR ENERGETICS

It is an experimentally observed fact that the mass of an atom is always lesser than the sum of the masses of its constituent particles such as protons, neutrons and electrons. Now the question arises why this mass defect occurs? And we also know that this mass deficiency is in the nucleus of an atom and has nothing to do with electrons. However, since tables of masses of isotopes include the electrons, we should also include them. The difference between the mass of an atom and the sum of the masses of its constituent particles is called the *mass defect*. The mass defect of an atom reflects the stability of the nucleus. It is equal to the energy released when the nucleus is formed from its constituent particles. The mass defect is therefore, also known as the *binding energy* of the nucleus.

For most naturally occurring isotopes, the mass defect is only about 0.15% or less of the calculated mass of an atom. A helium atom, for example, contains two protons, two neutrons and two electrons. The mass of a helium atom therefore should be 4.03296 amu.

2(1.00727) amu = 2.01454 amu

2(1.00866) amu = 2.01732 amu

Total mass = 4.03296 amu

When the mass of a helium atom is measured, one can find that the experimental value is smaller than the predicted mass by 0.03036 amu.

Predicted mass = 4.03296 amu

Observed mass = 4.00260 amu

Mass defect = 0.03036 amu

For $^{16}_{8}O$, this difference is 0.13709 amu.

What has happened to the mass represented by the mass defect?

In 1905 Albert Einstein postulated the special theory of relativity in which he stated that matter and energy are equivalent. This was the basis of our combination of the laws of matter and energy. This means that matter can be transformed into energy and vice versa. The first transformation occurs in the sun and other stars and was first accomplished on earth when controlled nuclear fission was achieved in 1939. The reverse transformation, energy into matter, has not yet been accomplished on a large scale. A Einstein stated that the equivalence between matter and energy could be related by simple mathematical reaction:

$$E = mc^2 \qquad (7.2)$$

Where E is the energy released, m is the mass transferred into energy and c is the velocity of light in vacuum (3.00×10^8 m/s). The binding energy serves the function for nuclear reaction that ΔH° does for the chemical reaction. It measures the difference between the stability of the products of the reaction and the starting materials.

A mass defect represents the amount of matter that would be converted into energy and released if a nuclide was formed from its initially separated nucleons. This energy is the nuclear binding energy. The binding energy can also he viewed as the amount of energy that must be added to take the nucleus apart to form isolated nucleus. It is therefore literally the energy that binds together the nucleons in the nucleus.

The binding energy of a nuclide can be calculated from its mass defect with Einstein's equation that relates mass and energy. For example, binding energy of helium nucleus can be calculated as follows:

Mass defect = 0.03036 amu

or Mass defect $= 0.03036 \times 1.66 \times 10^{-27}$ kg

$= 5.04 \times 10^{-29}$ kg ($\because$ 1 amu $= 1.66 \times 10^{-27}$ kg)

Velocity of light $= 3 \times 10^{8}\ \mathrm{ms^{-1}}$

$$E = mc^2$$

$$= 5.01 \times 10^{-29} \times (3 \times 10^{8})^2$$

$$= 4.53 \times 10^{-12}\ \mathrm{J}$$

Binding energies are usually expressed in units of electrons volts (eV) or million electron volts (MeV) per atom.

$$1\ \mathrm{eV} = 1.602 \times 10^{-19}\ \mathrm{J}$$

Hence $E = \dfrac{4.53\times10^{-12}}{1.602\times10^{-19}} = 28.30\times10^{6}$ eV/atom

or $E = 28.30$ MeV/atom

Obviously this much energy must be supplied to disrupt the nucleus of helium. (This has never been done).

Calculations of nuclear binding energy can be simplified by using the following conversion factor between mass defect (amu) and the binding energy is MeV.

$$1 \text{ amu} = 931.50 \text{ MeV} \tag{7.3}$$

Binding energies per nucleon are called average binding energies. For example, average binding energies of helium nucleus is 7.03 MeV.

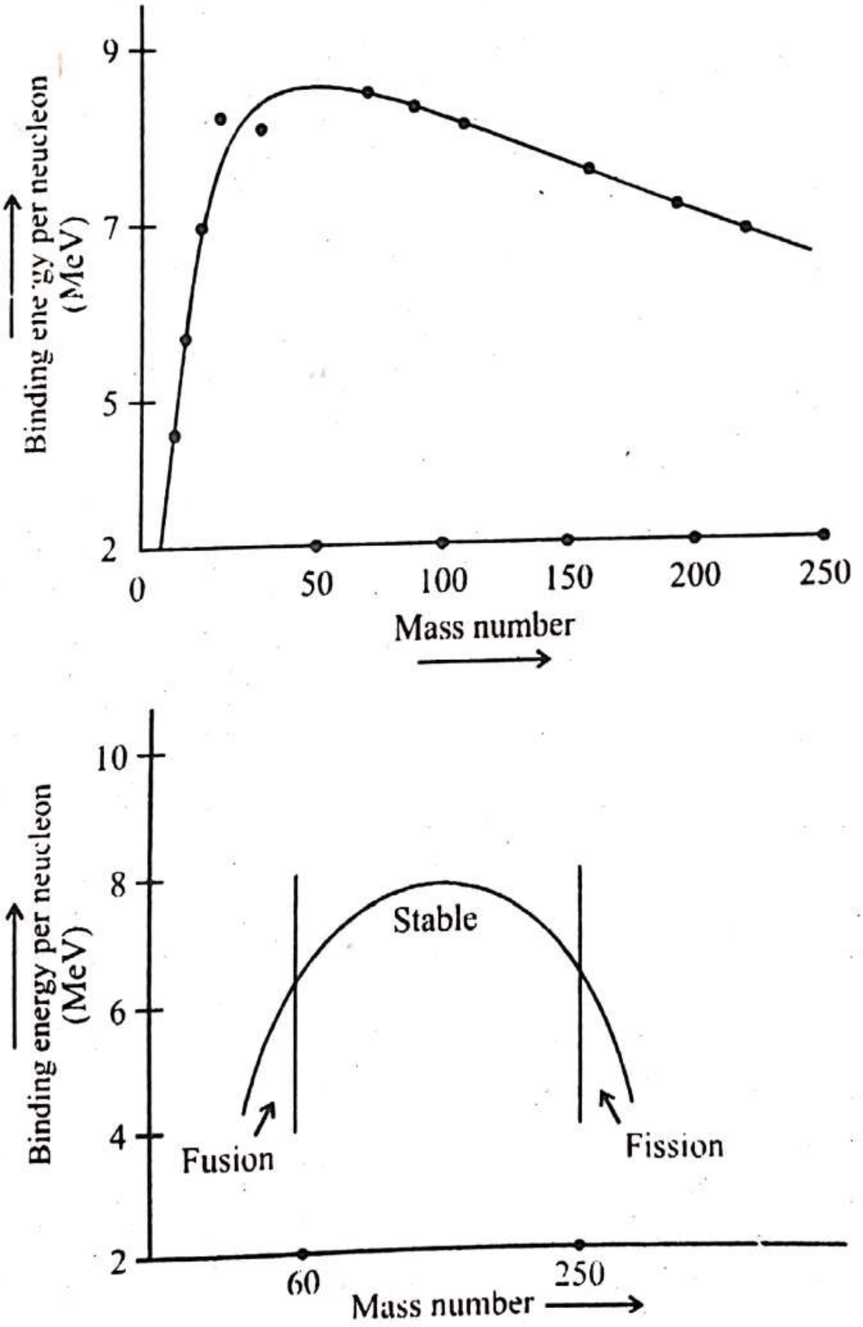


Fig 7.4. Average binding energies as a function of mass number

When N_A is the Avogadro constant (6.023×10^{23}).

The mass in gram of 1 amu is

$$= \frac{12}{N_A} \times \frac{1}{12} = \frac{1}{6.023 \times 1023}$$

$$= 1.66 \times 10^{-24} g$$

$$= 1.66 \times 10^{-27} kg$$

$$\therefore \quad E = mc^2$$

$$E = (1.66 \times 10^{-27} kg)(3.0 \times 10^8 m/s)^2$$

$$E = 1.492 \times 10^{-10} J$$

$$1eV = 1.66 \times 10^{-19} J$$

$$\therefore \quad \text{one amu} = \frac{1.492 \times 10^{-10}}{1.60 \times 10^{-19}} ev$$

$$= 9.315 \times 10^8 \text{ ev}$$

$$= 9.315 \times 10^2 \text{ MeV}$$

$$1 \text{ amu} = 931.5 \text{ MeV}$$

Example 7.4.

Calculate the binding energy per nucleon for ${}_2^4He$.

Solution:

The binding energy for ${}_2^4He$ is denoted by the equation

$$2n + 2p + 2\bar{e} \longrightarrow {}_2^4He \text{ (atom)} + \text{binding energy}$$

Sum of the masses of constituent particles on L.H.R. of the equation.

$$= 2(1.00866) + 2(1.00727)$$

$$= 4.03296 \text{ amu } (\therefore \text{ mass of } \bar{e} \text{ is ignored})$$

The actual mass of ${}_2^4He = 4.00260$ amu

$$\text{Mass defect} = 4.03296 - 4.00260 = 0.03036 \text{ amu}$$

$$\therefore \quad 03036 \text{ amu} = 0.30306 \times 931.5 \text{ MeV}$$

$$= 28.30 \text{ MeV}$$

There are 4 nucleons (2p + 2n) in the nucleus of ${}_2^4He$.

Therefore, the average binding energies is

$$= \frac{28.30}{4} = 7.07 \text{ MeV}$$

Example 7.5.

Masses of $_{3}^{7}\text{Li}$, $_{3}^{6}\text{Li}$ an $_{0}^{1}\text{n}$ are 7.016 amu, 6.015 amu and 1.0087 amu. Respectively. Calculate the binding energy of the $_{0}^{1}\text{n}$ in $_{3}^{7}\text{Li}$ in Mev.

Solution

Mass of $_{3}^{6}\text{Li}$ = 6.015 amu

Mass of $_{0}^{1}\text{n}$ = 1.0087 amu

Total mass = 7.0238 amu

Mass of $_{3}^{7}\text{Li}$ = 7.0160 amu

Mass defect = 7.0238 – 7.0160 = 0.0078 amu

B.E. of $_{0}^{1}\text{n}$ = 0.0078×931.5

= 7.265 MeV

7.10 NUCLEAR MODELS

In the case of nuclei, the law of force between the nucleons in not well understood. Thus we do not have any exact theory of the structure of a nucleus composed of Z protons and N neutrons interacting together with attractive exchange forces as will as electrostatic repulsions between the protons. The best way we can do is to work with simplified models known as *nuclear models*. The basic features of such models are that the nucleons maintain their identities in the nucleus and do not fuse together and the nucleons are bound by short range nuclear forces.

A nucleus consists of a number of particles in a small volume (nuclear diameter 10^{-13} cm or 10^{-15} m). The binding of such particles into a compound nucleus then involves very strong short range forces. In explaining the properties and behavior of a nucleus, various nuclear models have been proposed and attempts have been made to explain the various properties of the nuclei. We will discuss here only two important models.

1. The Liquid Drop Model:

The liquid drop model, also known as *point model*, was first proposed by Niels Bohr in 1936, and further developed by Bohr, Wheeler and independently Frenkel. It is largely based on the observation that nuclear volumes are roughly equal to the sum of the volumes of the individual particles. The nucleus can be considered as a bunch of particles which are bound together by mutual attraction in the same manner as drop of water is an aggregate of several water molecules which are held together by surface tension. As the size of drop increases, surface tension also increases and ultimately the drop disintegrates. Since the nuclear density from lighter elements (H and He) to heavier elements (U and beyond) remains as practically unaltered, it is reasonable to consider all the nuclei as a bunch of normal fundamental particles.

Thus nucleus can be considered as an incompressible liquid with very high density, greater than 10^{14} g/cc near its boiling point. As the nucleons are added to the nucleus (analogous to the situation when temperature of the drop is increased) the evaporation of the particles from the surface of the nucleus commences in the same way as that of the molecules from the surface of the liquid drop, the difference lies in the fact the characteristics of remaining molecules are different from the parent one whereas the remaining drop of the liquid is simply new form of the parent drop.

The liquid drop model has been employed with great success in the interpretation of intra-nuclear forces and of nuclear transformations. The merits of this model in the satisfactory explanation of various nuclear phenomena are given below

(i) It provides mechanism for low energy nuclear reactions.

(ii) The phenomenon of nuclear fission has been explained satisfactorily with the help of this model.

(iii) The calculation of nuclear binding energies and the study of properties of isobars have been made successfully on the basis of this model.

However, the liquid drop model has following limitation.

(i) This model does not explain satisfactorily the stability of the lighter elements, e.g. $^{2}_{1}H$, $^{6}_{3}Li$, $^{10}_{5}B$ etc.

(ii) This model is unable to explain nuclear isomers and abnormal high binding energies associated with certain magic numbers of either protons or neutrons. This led to the development of nuclear shell model in 1949.

2. Nuclear Shell Model:

This model was proposed by M.G. Mayer (1949) and modified by Haxel, Jenson and Suess in 1950. The model presents a systematic form of nuclear model. The shell model is based on the fact that the nucleons (proton + neutron) are distributed in a number of discrete energies levels or shells satisfying certain quantum mechanical conditions. Each shell or level accommodates a definite number of nucleons of one kind (either proton or neutron) and is regarded as the closed or filled shell. Thus protons and neutrons are arranged is separate closed or filled shells. These closed shells allow the spin-orbit coupling of each individual nucleon in a shell but no interactions with nucleons of the other shell. This model could explain successfully the nuclear properties such as stability, abundance, binding energy, spin, magnetic moment etc. of certain nuclides containing the definite number of nucleons, namely, 2,8,20,50,82 and 126. Since these nucleon numbers apparently represent closed shells in the nucleus, model is also referred to as *nuclear shell model*.

The correlation between various nuclear properties and the magic numbers indicates the possibility of shell structure in the nucleus. According to the shell model, protons and neutrons are arranged into separate shells within the nucleus, like electrons in an atom. We know that in atoms, each shell accommodates a certain maximum number of electrons, viz, 2,10,18,36,54 and 86, and is regarded as a *filled or closed shell*. In an analogous manner, protons and neutrons form separate closed shells within the nucleus when their number equals, 2,8,20,50,82 and 126. These numbers are reformed to as *magic numbers*. Nuclei having filled shells are more stable than the nuclei with unfilled shells.

The existence of magic numbers has been interpreted as an indication of a shell structure in the nucleus. The shell model compares the nucleus to a shell made of independent particles with small interactions caused by their movement in a common field of force. The nucleons are assumed to move in a definite orbits outside the nucleus and to have very little interaction with each other. They also obey Pauli's exclusion principle, according to which no two nucleons can have the same values of four quantum numbers.

According to shell model, in an even-even nucleus, the protons and neutrons should remain as paired resulting in the cancellation of one another's spin and orbital angular moment and hence such nuclei should have resultant nuclear angular moment equal to zero. As even-odd or odd-even nucleus should give half integral angular momentum and an odd-odd nucleus should yield integral total angular momentum. These observations are in good agreement with the experimental data.

The shell model has the following merits.

(i) This model has been applied successfully to explain many nuclear properties such as stability, binding energies, relative abundance, neutron absorption cross section etc. of nuclei at nucleon magic numbers.

(ii) The spin and parity of odd mass number nuclides can be determined from the odd nucleon in nuclei.

(iii) The correlation of the nuclear isomerism with magic numbers has been interpreted in terms of shell model.

(iv) The magnetic moments of odd-A nuclides depend on the single unpaired nucleon. The identical spins and closely similar magnetic moments for certain groups of two or three isotopes with odd-A and odd-Z have been explained on the basis of shell model. For example, ${}^{107}_{47}Ag$ and ${}^{109}_{47}Ag$

The basic idea of shell model is that the nucleons behave as though they were confined in a common potential well and they interact with each other only slightly. This is directly opposed by the liquid drop model, which implies a strong interaction. Shell model is, however very useful in β-decay, in isomerism study and nuclear reaction studies.

7.11 RADIOACTIVITY

The phenomenon of radioactivity was discovered by H.Becquerel in 1895. He observed that when a photographic plate wrapped in black paper was exposed to certain uranium salts, it was fogged. He concluded that fogging of the plate was due to the radiation emitted from the uranium salt. Subsequently, it was shown that radiation can cause ionization of air and is not affected by factors like temperature, pressure, chemical environment or source of uranium. The spontaneous emission of radiation of this type by an element is called radioactivity and the element which exhibits this behavior is said to be radioactive. The name radioactivity was proposed by a Polish pupil of Becquerel, Marie Sklodowska, who later became the illustrious scientist Marie Curie, the recipient of two Nobel Prizes.

In 1898, Marie and her husband Pierre Curie undertook the systematic study of radioactivity of many substances. They noted that the chief source of uranium (pitchblende, U_3O_8) contains elements which had greater activity than uranium. By chemical methods, Madam Curie succeeded in isolating from this mineral two new radioactive elements polonium and radium. At the same time Madam Curie (France) and G.C. Schmidt (Germany) independently discovered a new radioactive element, thorium. Debierne in 1899 discovered a new element actinium which was also radioactive. Since then, the systematic investigation has been brought to light about forty elements which show characteristics of radioactive elements. A large number of other elements have found to become radioactive by special methods.

In 1902, Rutherford began investigating the nature of the radiations emitted from radioactive elements. He showed that the radiations were composed of three types of rays; the alpha rays (α) the beta rays (β) and the gamma rays (γ). Characteristic properties of these three types of radiations are given below:

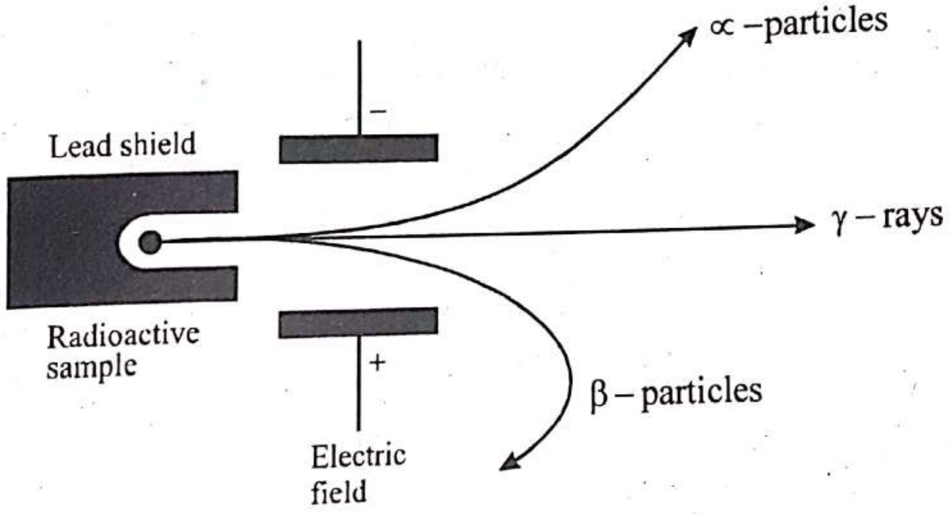


Fig 7.5. The effect of an electric field on α, β and γ rays.

Alpha Rays

(i) **Nature:** The deflection of α – rays in an electric or a magnetic field shows that these are positively charged particles. Furthermore, it has been shown by Rutherford and T. Royds (1909) that an alpha particle carries two units of positive charge and has a mass approximately four times than that of the hydrogen atom. In other words the α – particle is a helium nucleus consisting of two neutrons and two protons (^4_2He).

(ii) **Velocity:** Alpha particles generally move with a velocity ranging from 1.4 to 2.0×10^7 ms^{-1}.

(iii) **Ionization:** Since alpha particles have large mass and move with high speeds, they have therefore, considerable kinetic energy. Due to this large energy, the alpha particles cause ionization when passed through a gas.

(iv) **Luminescence:** The $\alpha-$particles cause luminescence when they strike a zinc sulphide screen, and have intense photographic activity.

(v) **Penetrating Power:** Alpha particles have smaller penetrating power and are stopped by a sheet of paper or by a thin foil of aluminum or a few cm of air at atmospheric pressure.

Beta Rays

(i) **Nature:** The deflection of $\beta-$particles in an electric or a magnetic field shows that they are negatively charged particles. Their e/m ratio is the same as that of the electron indicating $\beta-$particles are actually fast moving electrons.

(ii) **Velocity:** The velocity of $\beta-$particles is approximately equal to that of light. The average value being 2×10^8 ms^{-1}.

(iii) **Ionization:** Due to smaller mass, $\beta-$particles have low ionization power than $\alpha-$particles.

(iv) **Luminescence:** Due to their low kinetic energy, $\beta-$particles have very little effect on zinc sulphide plate. On the other hand, their photographic activity is greater than that of $\beta-$particles, perhaps; it is due to the production of X-rays being produced by the absorption of $\beta-$particles, by matter.

(v) **Penetrating power:** Due to their high speed, $\beta-$particles are more penetrating than $\alpha-$particles. Their penetrating power is about 100 times more than those of $\alpha-$particles. $\beta-$rays are stopped by 3 mm of lead. Because of their small mass they are easily deflected from their path by an electric or a magnetic field.

Gamma Rays:

(i) **Nature:** Gamma rays are uneffected by electric and magnetic fields, hence they are not charged particles. They are electromagnetic radiations analogous to X-rays. Their wavelengths lie in the range of 10^{-10} to 10^{-13}m and hence have shorter wavelengths than X-rays.

(ii) **Velocity:** They travel with extremely high velocity, which is nearly equal to that of light.

(iii) **Ionization:** They cause ionization of the gases, but have proportionally weaker ionizing power, among the three radiations.

(iv) **Penetrating power:** Gamma rays have very high penetrating power due to very short wavelength. Their penetrating power is about 10 to 100 times more than $\beta-$ rays. These rays are stopped by several centimeters of lead.

(v) **Luminescence:** Gamma rays produce very little effect on zinc sulphide and photographic plate.

7.12 DETECTION AND MEASUREMENT OF RADIOACTIVITY

Decaying of a radioactive material in unit time is called its activity. The standard unit of radioactivity is Curie (Ci), which is defined as that amount of any radioactive material which gives 3.70×10^{10} disintegrations per second. The disintegration per second is abbreviated as dps. One gram of radium-226 undergoes 3.70×10^{10} disintegrations per second and is also equal to one Curie. In practice, activities are expressed in terms of megacuries, curies, millicuries and microcuries.

1 curie (Ci) $= 3.70 \times 10^{10}$ dps

1 millicurie (mCi) $= 3.70 \times 10^{7}$ dps

1 micrcocurie (μCi) $= 3.70 \times 10^{4}$ dps

The SI unit of radioactivity is Becquerel (Bq) which is defined as the activity due to one disintegration per second.

1 Ci $= 3.70 \times 10^{10}$ Bq

1 Bq = 1 disintegration per second.

The activity of a radioactive material per unit mass is called its specific activity. It is measured in counts per second or counts per minute. It is a measure of relative abundance of radioisotopes, since radioisotopes occur in mixture with stable isotope.

The detection and measurement of radioactivity of any sample is based on the detection, identification and measurement of the radiations emitted by the sample. Some methods employed for the purpose are described below:

(i) Photographic Methods.

(ii) Gas Ionization Methods.

(iii) Scintillation Methods.

1. Photographic Methods:

Detection of radiation by photographic method is also known as autoradiography. Autoradiography is a photochemical process. It was the one used by Becquerel in 1896 in the discovery of radioactivity. In this method, ionizing radiation interacts with the silver halide in photographic emultion. When a radioactive material is placed near photographic film or plate, a blackening will be produced on development of the emulsion. The blackened areas constitute a self-portrait of the activity in the material. The intensity of the blackening (as determined by an eye or with a densitometer) at a given place will be a function of exposure time and the amount of activity in the sample at that place.

The method of autoradiography is particularly suitable when the distribution of a radioactive compound in biological material is to be studied. However, precautions should be taken that there is no chemical or pressure effect of the material on the emulsion as this may also produce an image. Autoraidography is frequently applied to the determination of the components of a paper or thin layer chromatogram, but detection of radiation on a quantitative basis by this method is difficult and tedious.

2. Gas-Ionization Methods

When radiation passes through a gas, some of the energy is transferred to the gas molecules, which may be ionized into positive ions and electrons. If an electric field is applied, these ions and electrons can be collected before they have the opportunity to recombine (Fig. 7.6). The magnitude of the resulting current can be correlated with the amount of radiation initially responsible for the ionization. An ionization chamber is a device in which an electric field is applied just sufficient to collect all the ions and electrons produced in the volume of the gas between the electrodes.

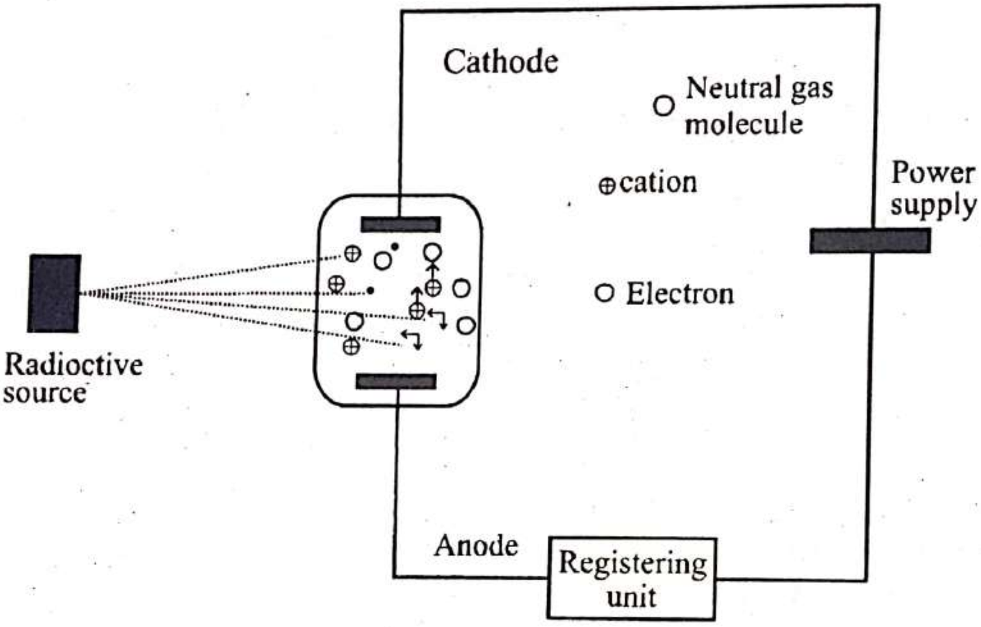


Fig 7.6. Radiation detection by ionization.

A common gas ionization counter is the Geiger Muller Counter which is shown in Fig. 7.6 In fact, it is also an ionization chamber in which the cathode is cylindrical and a thin tungsten wire fixed along the axis of the cylinder or tube shell serves as anode. Radiation enters the tube through a thin window made of mica. The tube is filled with a gas, usually argon at low pressure. A working potential of about 1200 volts is applied between the inner wire and the outer tube. When ionizing radiation enters through thin mica window, interacts with the filled gas to produce positive ions and electrons. The positive argon ions (Ar+) move to the cathode and the electrons to the anode. The counter generates a pulse due to the free electrons. Amplification of the pulse from each ionization causes a clicking sound in a loudspeaker or activates a digital counter that registers the amount of radiation entering the tube. A chart recorder may also be attached to the circuit to give a graphic display of the intensity of radiation versus time. This counter is generally employed for the detection of β and $\gamma-$ rays, although its modified form could be used for $\alpha-$particles, protons, neutron and X-rays photon.

Merits

(i) This technique is very sensitive.

(ii) It produces a large pulse which requires no further amplification.

(iii) The pulse size is independent of the nature of incident radiation.

Limitations

(i) It is very sensitive for very high counting rates.

(ii) It is unable to give information about the nature of particle detected.

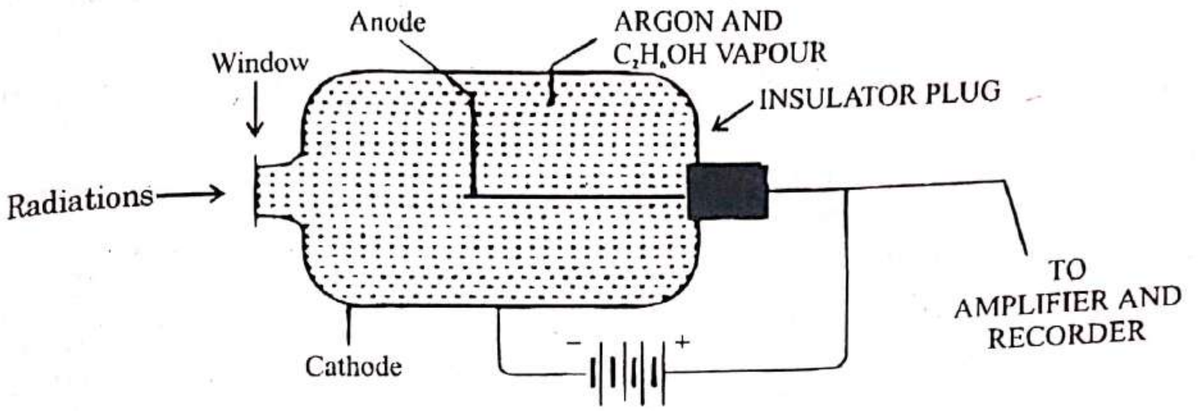


Fig 7.7. The G.M. Counter

3. Wilson's Cloud Chamber

Wilson developed a cloud chamber in which the tracks of charged particles can be seen. The principle of this technique is that when a gas containing vapours at saturation pressure is expanded suddenly it gets cooled and becomes supersaturated. In presence of dust particles, droplets are formed around the dust particles. In a dust free atmosphere condensation could be produced on a negative ion present in the gas and expansion of gas is made 1.31-1.4 times its volume.

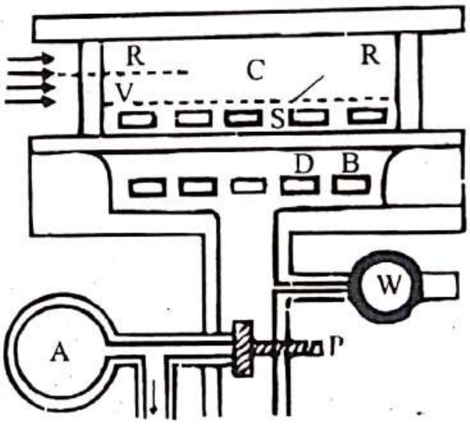


Fig. 7.8. Wilson's Cloud Chamber

The Wilson's Cloud Chamber consists of a cylindrical glass chamber, C. It is provided with a glass plate cover and a perforated metal plate base. The metal plate is covered by a dark velvet cloth V. Water is sprinkled on velvet cloth to provide water vapour to saturate the air in the chamber, C. The rubber diaphragm D forms an air-tight seal between chamber C and space S below it, A is an evacuated container kept closed by a piston P Fig 7.8.

When a piston P is withdrawn, the space S is connected to the container A. The pressure in S suddenly falls. This pulls down the diaphragm D, and the air in the chamber C undergoes expansion. After expansion, container A is closed by the piston P and air is slowly admitted into the space S through a small valve V. The diaphragm R goes to its original position. The pressure in the chamber C reverts to its original value. The second perforated plate B is kept below the diaphragm D and expansion ratio adjusted.

The water droplets are condensed on charged ions. The Chamber is illuminated and tracks can be viewed through the top glass plate and photographed. After that potential difference is adjusted to 100V and electric field sweeps the ions from the chamber. The chamber is then made ready for next operation.

Alpha-particles ionize to large extent and produce thick tracks. Beta particles ionize to less ionization and tracks are thin.

Demerits

1. It is not practicable to build Cloud Chamber large enough to show the entire path of an extremely high energy particle.
2. High energy bubble chambers or photographic emulsions have to be used to observe the tracks.
3. The Cloud Chamber is less sensitive as the duration of super saturation is of the order of one second.

4. Scintillation Methods

A scintillator is a substance which emits a small flash of light when struck by a fast charged particle. Solid scintillators are particularly suited for the detection of gamma rays because of high density and high atomic number of the crystals used. Some alkali halides, in particular sodium iodide (activated with Tl) have been the most useful.

When a gamma photon is partially or totally absorbed in the scintillation crystal, at least one fast electron is liberated (photoelectron, Compton electron or pair production electron). The electron causes ionization and excitation along, its path in the crystal. When the excited atoms return to their ground state, they emit light photons, the number being proportional to the gamma photon energy that is absorbed by the crystal.

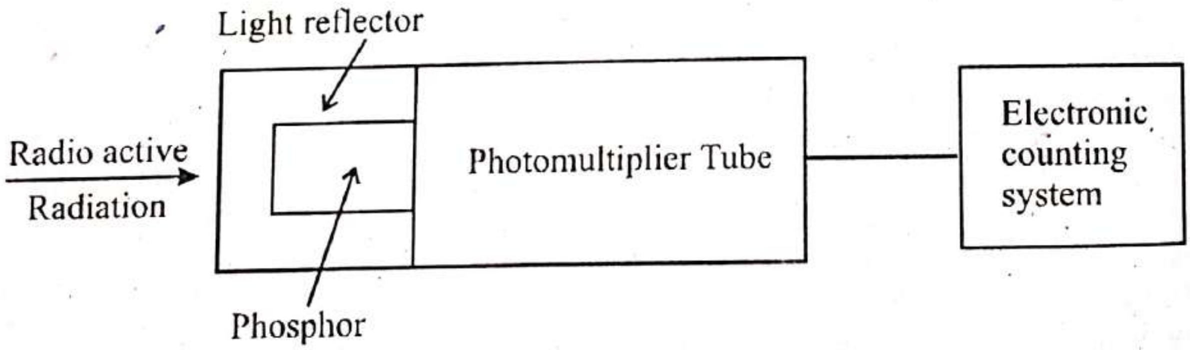


Fig. 7.9. Scintillation counter

In the so-called photo multiplier tube, a photosensitive layer or photocathode is optically coupled to the scintillation crystal. The light flashes produced in the crystal cause electrons to be liberated from the photocathode. The photocathode is followed by a series of electrode stages (dynodes), each at a potential more positive than that of the preceding one. Thus photoelectrons released from the photocathode surface will be attracted to the first dyode and will gain sufficient kinetic energy to release several secondary electrons from the surface. This multiplication process occurs at each stage and at the end of ten or more stages a very large number of electrons will arrive at the anode. The size of this pulse of electrons will be proportional to the original gamma ray energy absorbed in the crystal.

7.13 INTERACTION OF IONIZING RADIATION WITH MATTER

Radiation chemistry deals with the study of chemical changes produced in a substance by the action of ionizing radiations. The common ionizing radiations are electromagnetic high energies radiations X-rays, gamma rays and carpuscular high energies radiations such as electrons protons, neutron, electrons, alpha particles, nuclear fission fragments, recoil nuclei resulting from nuclear reactions, fluxes of accelerated multiple charged ions etc. Radioactive substances possess natural ionizing radiation.

Protons, electrons, alpha-particles and heavier charged particles are deaccelerated on interaction with a substance at energies used in radiation chemistry. This is mainly due to interaction with atomic electrons of that substance. This process results in the ionization of the atoms and the molecules of the medium as well their excitation. High energies electrons lose their energies because of inelastic scattering on the electrons and atomic nuclei of the medium, which leads to the ionization of atoms and molecules.

X-rays and gamma rays lose their energies through photoelectric absorption, i.e., through photoelectric effect, Compton scattering, the formation of position-electron pairs (pair production). The pair production process is accomplished for protons with energies 1.02 MeV. The atoms of the medium get ionized in case of photoelectric absorption and Compton scattering.

Neutrons only interact with atomic nuclei. This interaction involves elastic and inelastic scattering, nuclear reaction with the emission of charged particles or photons and nuclear fusion also. Maximum loss in energy occurs as atoms with a mass equal to the mass of a neutron, i.e., an hydrogen atoms. in elastic scattering, an excited recoil nucleus is formed. The latter is stabilized through the emission of a gamma ray.

Nuclear reactions and nuclear fission are accompanied by the emission result of fast heavy charged particles or photons of high energy. All these processes in the ionization and excitation of atoms and molecules of an energy absorbing medium. An interesting point about radiation chemistry is that the out come of an ensuring chemical reaction may depend, not only on the material irradiated, but also upon the type of radiation used. This is due to the fact that different types of radiation will produce different concentration of the activated species. Alpha particles, with their high energy and short range, produce a much greater concentration of ions and excited molecular species which interact with one another, than do $\beta-$particles which have a much longer path.

All types of ionizing radiation initiate two principal primary processes.

(i) The ionization of molecules (atoms)

$$M \longrightarrow M^{+} + e^{-}$$

(ii) The excitation of molecules (atoms)

$$M \longrightarrow M^{*}$$

These primary processes are almost independent of the type of the substance and generally a pair of ions is formed for every 34 eV of absorbed energy. The positive ions, excited molecules and electrons having thermal velocities, these participate in secondary chemical process, which depends on the kind of radiation or ionization density, its intensity and the composition of the irradiated material. Unstable molecular ions decompose into a free radical and an ion or some times into a stable molecular ion and another molecule.

$$M^+ \longrightarrow R_1 + R_2^+$$

$$M^+ \longrightarrow M_1^+ + M_2$$

Stable positively charged ions can interact with the surrounding molecules with transfer of charge or formation of new ions and radicals through ion-molecule reactions.

$$M^+ + M_1 \longrightarrow M_1^+ + M_2$$

or $$M^+ + M_1 \longrightarrow R_1^+ + R_2$$

Slowed down electrons neutralize positive ions or are capture by molecules having great electron affinity.

$$M^+ + \bar{e} \longrightarrow M^*$$

$$M + \bar{e} \longrightarrow M^-$$

$$M + \bar{e} \longrightarrow M_1 + M_2^-$$

Negative ions recombine with positive ions, forming the excited molecules.

$$M_1^+ + M_2^- \longrightarrow M_1^* + M_2$$

The negative ions can also undergo reaction similar to those of positive ions. Excited molecules undergo decomposition into stable molecules, radicals and ions.

$$M^* \longrightarrow M_1 + M_2$$

$$M^* \longrightarrow R_1 + R_2$$

$$M^* \longrightarrow M_1^+ + M_2^+$$

The excited states can be stabilized through fluorescence or conversion of the energy of electrons into vibrational energy of molecules due to inter molecular transfer of energy. This energy transfer may take place either by direct collision with an unexcited molecule or by electromagnetic interaction at a distance. The active radicals, ions or molecules formed in the secondary processes also interact with the surrounding molecules of the medium and leads to the occurrence of many chemical processes.

In most pure form the above processes take place in the gas phase, where excited molecules may exist for a long time and as a result dissociation becomes highly probable. In liquid phase ion-molecules reactions are more probable while in a condensed phase, the recombination of ions and radicals become more probable. In molecular crystals, the stabilization of excited states is similar to the processes occurring in non-polar liquids. In ionic-crystals, neutralization of ions occurs without displacement of atoms from lattice points with the formation of various types of lattice imperfection.

7.14 RADIATION DOSIMETRY

We know that the radiation loses its energy by interaction with matter. The energy loss can be quantitatively measured. The energy loss is generally expressed in terms of quantity of radiation energy absorbed. The determination of this quantity constitute *radiation dosimetry*. Before we describe the method for measurement of the quantity of radiation, it is essential to consider the units employed for expressing the radiation energies absorbed by the matter.

Units of Radiation Energy:

The amount of energy absorbed is usually called the dose. The dose is generally expressed in terms of total ionization produced in a given volume of air or other substance. Several units have been adopted to express the absorbed dose. The absorbed dose of any ionizing radiation in the energy absorbed per unit mass of the irradiated material. The unit of absorbed does is the rad; 1 rad is 100 ergs per gram of the material. The SI unit for absorbed dose is joule per kilogram (J kg^{-1}) which is given the special name Grey (symbol, Gy).

$$1 \text{ rad} = 0.01 \text{ Gy} = 0.01 \text{ J kg}^{-1}$$

The *absorbed dose rate* is the absorbed dose per unit time and has the units Grey per unit time (Gys^{-1}). The absorbed dose is a direct measure of the energy transferred to the irradiated material that is capable for producing chemical or physical change, it is determined both by the characteristics of the radiation field and the composition of the stopping material.

The measurement of radiation dose-either absorbed dose or exposure dose can be carried out by primary or absolute and secondary methods. Primary methods involve direct determination of exposure or absorbed dose from physical measurements of the energy absorbed (by calorimetry), the ionization produced in a gas, or the charge carried by a beam of particles of known energy. Primary dosimeter, are often not suited to routine use and in practice secondary dosimeter, (e.g. thimble ionization chambers and chemical dosimeters) whose response to radiation is known from comparison with primary dosimeter, an generally used. We will discuss only these two methods.

1. Ionization Chambers:

Measurement of ionization produced in a gas by radiation have been used for the purpose of dosimetry since the discovery of X-rays. Ionization dosimeter retains its position because of its convenience and accuracy for measurements of exposure and absorbed dose ionization is measured by means of an ionization chamber (which may be either primary) or a secondary instrument) consisting of two electrodes separated by a gas filled space in which the incident radiation produces ionization. A potential is applied to the electrodes to attract the ions to them and the resulting current or the discharge of electrodes is measured by some appropriate means. The quantity obtained in this way is the exposure, from which the absorbed dose can be calculated if the composition of the medium and energy or energy spectrum of the radiation is known.

In the absolute ionization measurements, i.e., in the wall-less air filled chambers, there are some practical difficulties as to the collection of all the ions and to the uniformity of the electrical field, producing the electronic equilibrium in the air.

The most frequently used secondary type is the air wall chamber in which small volume of the air is surrounded by a much thinner layer of the solid material with the same chemical composition as air, referred to an air equivalent material such as Bakelite, Lucite and Nylon. The ionization produced per unit mass of air is therefore, exactly the same as that produced by the same flux of X-rays or gamma rays in a wall-less chamber. Ionization chambers of secondary types are to be standardized at different wave lengths by the use of standard "wall-less" chambers.

Thimble ionization chambers are included in this type of secondary dosimeter. The thimble ionization chamber is the Victorian condenser meter in which a small volume of the air is enclosed by a Bakelite cap, which is made conducting on the inside by coating of colloidal carbon, and in the center is an aluminum electrode insulated from the cap. The exposure dose of X-rays or gamma rays can be measured conveniently by the use of this ionization chamber.

The absorbed dose, D_A, in dry air, or equivalent material, exposed to X-rays or gamma radiation and in electronic equilibrium can be calculated from the observed exposure, X_A, if the mean energy require to form an ion-pair in air, Wair, is known.

$$D_A = \frac{X_A (\text{C kg}^{-1}) \text{ Wair (J)}}{e(\text{C}^{-1})} \text{ Gy} \qquad (7.3)$$

where e is the charge on electron. the quotient X_A/e measures the number of ion pair, each formed by the energy absorption of Wair. Wair is generally used in eV. Thus

$$D_A = \frac{\text{C}}{\text{kg}} \times 6.2415\text{J} \times 10^{18} \frac{\text{electron charges}}{\text{C}} \times 33.85 \frac{\text{eV}}{\text{ion pair}} \times 1.6022 \times 10^{-19} \frac{\text{J}}{\text{eV}} \times 1 \frac{\text{GY}}{\text{J/kg}}$$

$$D_A = 33.85 X_A \text{ Gy} \qquad (7.4)$$

2. Chemical Desimetery:

In the preceding section, we saw that the radiation dose from ionizing radiations can be measured approximately by employing physical methods which consist of measuring the ionization produced in a gas. It is however, possible to determine directly the energy absorbed by measuring the radio chemical yield in some appropriate system. We confine our interest here to chemical dosimetry. In chemical dosimetry the absorbed dose is determined from the chemical change produced in a suitable substance. Calculation of the absorbed dose requires a knowledge of the radiation chemical yield (G) for the reaction or product measured, which is found by comparing the chemical system with some form of physical (absolute) dosimeter. A common quantitative measure of the efficiency of the radiation chemical effect is the number of molecules transformed for each 100 eV of energy absorbed, called the G *Value of the reaction*. Chemical dosimeters are therefore, secondary dosimeters, used because of their greater convenience. The quality they measure is the average absorbed dose in the material composing the dosimeter. Generally aqueous dosimeter are used of the sample is an aqueous solution, a biological material, or an organic substance.

Due to large number of chemical systems that may be used for chemical dosimetry, it is useful to list some desirable features in a chemical desimeter;

(i) The magnitude of the chemical change should be proportional to the radiation dose over, a wide range of dose, and independent of dose rate, of the energy and intensity of the radiation, and of temperature.

(ii) It is desirable that the system should be relatively insensitive to the presence of impurities and to the nature of containing vessel.

(iii) A chemical dosimeter should be stable under normal conditions and reproducible.

(iv) It should be simple to use.

(v) The dosimeter should be easy to prepare from standard shelf regents and solvents.

(vi) The response should not be dependent on minor changes in the composition of the dosimeter, e.g. upon small changes in the concentration of reagents or pH of the solution.

In practice no one dosimeter fulfills all these requirements. Of the chemical systems the Fricke, or ferrous sulfate dosimeter is the most frequently used dosimeter which comes closest to meet these requirements. At present this is the best and most widely used chemical dosimeter. Other systems may be superior for some purposes.

Fricke (Ferrous sulfate) Dosimeter:

This consists in measuring the extent of oxidation of an acid solution of ferrous sulfate to ferric salt, in the presence of oxygen and under the influence of radiation. The standard dosimeter solution contains 1×10^{-3} M ferrous sulfate or ferrous ammonium sulfate, 1×10^{-3} M NaCl in 0.4 M H_2SO_4 (pH 0.46) and is saturated with air (the concentration of oxygen is about 2.5×10^{-4} M); the concentration of the reagent is not critical and small variations in above values are acceptable.

However, the solution slowly oxidizes and should not be stored for more than a few days. Fricke proposed this system as an X-ray dosimeter, choosing 400 mol m^{-3} H_2SO_4 as solvent so that the response to X-rays should be same as that of standard air ionization chambers over a range of X-rays energies. To protect oxidation of ferrous ions against sensitization by organic impurities, NaCl is added to the dosimeter solution. But the addition of NaCl is not necessary if both the water and the reagents used are purified exhaustibly.

To determine the absorbed dose, a sample of Fricke solution in a thick container is exposed to the radiation at the desired spot for a measured length of time and the yield of Fe^{3+} ions is measured specterophotometrically at 304 nm (λ max for Fe^{3+} ions). The relative extinction coefficients may be taken $\in(Fe^{3+}) = 220.5 \pm 0.3 m^2 mol^{-1}$ and $\in(Fe^{2+}) = 0.1 m^2 mol^{-1}$, or the resulting concentration of Fe^{3+} ions may be determined by comparing the optical density of irradiated and non-irradiated dosimeter solutions at 304 mm at which Fe^{3+} ions should have maximum absorption with respect to concentration of Fe^{3+} ions. For any dosimeter in which radiation induces a chemical change, the mean absorbed dose (D_D) over the volume occupied by the dosimeter is given by

$$D_D = \frac{\text{yield of radiation induced product (mol/kg)}}{\text{radiation chemical yield (mol / J)}} \text{ Gy} \qquad (7.5)$$

7.15 RADIOACTIVE DECAY

Radioactive or nuclear decay is a process in which a parent nuclide disintegrates into daughter nuclide(s) with the emission of radiation or particles. In the preceding sections, we learnt that the radioactive elements undergo spontaneous transformation accompanied by the radiations. This transformation is related to the nature of radioactivity and termed as the *disintegration (decay) process*. For a particular atom of a radioactive element to disintegrate the length of the time interval is of importance. The disintegration of radioactive element for unit interval of time, i.e., the rate of disintegration is of great help to determine and identify the radioactive species.

While discussing the nuclear stability, it was seen that only certain combinations of protons and neutrons produce stable nuclei, whereas others do not. Unstable nuclei decay by emitting alpha (α), beta (β) and gamma (γ) radiations. The emission of these radiations by unstable nuclei in their decay process is called *radioactivity* and the decay process is called *radioactive decay*. Radioactive decay or radioactivity is not influenced by chemical or physical means, i.e., we can neither retard nor accelerate the rate of radioactive decay by use of heat, pressure, electric fields etc. Not all the three radiations (α, β and γ) are emitted by the same nuclide in radioactivity. Usually a radioactive nuclide emits $\alpha-$particles and $\gamma-$rays or $\beta-$particles and $\gamma-$rays. Of course there are several exceptions to this rule, like $^{3}_{1}H$, $^{14}_{6}C$, $^{32}_{15}P$ etc. These nuclides emit only $\beta-$rays and are called pure $\beta-$emitters.

There are various processes by which an atom can alter its proton-neutron ratio or decrease its atomic number. Following are some of the important modes of nuclear decay.

1. Alpha Particle Decay

The $\alpha-$particle is made up of 2 protons and 2 neutrons. Its charge number is 2 and mass number is 4. Therefore, if a nuclide emits $\alpha-$particles, its charge number is reduced by 2 and mass number by 4, because both the charge and mass numbers are conserved during the nuclear transformation. Alpha decay can be expressed by the following generalized equation.

$$^{A}_{Z}X \longrightarrow {}^{A-4}_{Z-2}Y + {}^{4}_{2}He + Q$$

Where Q is the amount of energy released in α – decay. This energy is shared between α – particles and the residual nuclide in accordance with the laws of conservation of energy and momentum. During α – decay, the daughter nucleus shifts 2 places to the left in the periodic table.

All nuclides with atomic number greater than 83 are radioactive and are located beyond the band of stability. Many such nuclides (with few exaptions) decay by α – commission. This is not unexpected, because α – particle is relatively large particle and a nucleus which emits such a particle must itself be large. Some examples of α – decay are given below:

$$^{238}_{92}\text{U} \longrightarrow {}^{234}_{90}\text{Th} + \propto$$

$$^{226}_{86}\text{Ra} \longrightarrow {}^{222}_{86}\text{Rn} + \propto$$

$$^{210}_{84}\text{Po} \longrightarrow {}^{206}_{82}\text{Pb} + \propto$$

$$^{239}_{94}\text{Pu} \longrightarrow {}^{235}_{92}\text{U} + \propto$$

$$^{204}_{82}\text{Pb} \longrightarrow {}^{200}_{80}\text{Hg} + \propto$$

Some of the isotopes of uranium (Z = 92) and elements of higher atomic number, (the transuranium elements) also disintegrate via spontaneous nuclear fission in which a heavy nucleus splits into nuclides of intermediate masses and neutrons.

2. Beta-Particle Decay

There are several decay processes which come under the heading of beta-decay.

(i) Emission of electron by the nucleus or β^- – decay

(ii) Emission of positron by the nucleus or β^+ – decay .

(iii) Electron capture by the nucleus.

(i) β^- – decay :

We know that electron (negatron) and positron do not constitute the nucleus. How then are they emitted by the nucleus? They are created in the nucleus only at the time of emission. When a nucleus has an excess of neutrons than required for stable nucleus in a particular region, then it will be unstable because of the deficiency of protons. Such a nucleus will achieve stability by changing its neutrons to protons. It is represented in the following way:

$$n \longrightarrow p + \beta^- + \upsilon^- \text{ (antineutrino)}$$

The daughter nucleus, thus, formed is shifted one place to the right in the periodic table. β^- – decay can be represented by the generalized equation.

$$^{A}_{Z}X \longrightarrow {}^{A}_{Z+1}Y + \beta^- + \upsilon^- + Q$$

The energy Q released in the process is shared between the electron and antineutrino and they carry away part of energy. β^- – particles may have energy between zero and certain maximum value.

β^- – decay is common over the entire range of nuclides and amongst the naturally occurring heavy radioactive nuclides and in fission products. Some common examples are:

$$^{28}_{88}\text{Ra} \longrightarrow {}^{228}_{89}\text{Ac} + \beta^-$$

$$^{234}_{90}\text{Th} \longrightarrow {}^{234}_{91}\text{Pa} + \beta^-$$

$$^{14}_{6}\text{C} \longrightarrow {}^{14}_{7}\text{N} + \beta^-$$

$$^{32}_{15}\text{P} \longrightarrow {}^{32}_{16}\text{S} + \beta^-$$

$$^{24}_{11}\text{Na} \longrightarrow {}^{24}_{12}\text{Mg} + \beta^-$$

Number of neutrons can also be decreased (less common) by *neutron emission*. It simply decreases the number of neutrons by one, without changing the atomic number. A light isotope is formed.

$$^{137}_{53}\text{I} \longrightarrow {}^{136}_{53}\text{I} + \text{n}$$

$$^{17}_{7}\text{N} \longrightarrow {}^{16}_{7}\text{N} + \text{n}$$

(ii) β^+ – decay:

When a nucleus has more protons than permitted by neutron: proton ratio for stable nuclide in certain region it will be unstable. Such a nucleus will achieve stability by converting its protons into neutrons.

$$\text{P} \longrightarrow \text{n} + \beta^+ + \upsilon \text{ (neutrino)}$$

A positron has the mass of an electron, but a positive charge. Positron decay can be represented by the following generalized equation.

$$^{A}_{Z}\text{X} \longrightarrow {}^{A}_{Z-1}\text{Y} + \beta^+ + \upsilon + \text{Q}$$

The energy released during β^+ – decay is shared between β^+ and υ particles. By changing a proton into neutron, positron emission results in a decrease in the atomic number and increase in the number of neutrons by one, without any change in the mass number. Some examples of β^+ – decay are given below.

$$^{38}_{19}\text{K} \longrightarrow {}^{38}_{18}\text{Ar} + \beta^+$$

$$^{15}_{8}\text{O} \longrightarrow {}^{15}_{7}\text{N} + \beta^+$$

$$^{22}_{11}\text{Na} \longrightarrow {}^{22}_{10}\text{Ne} + \beta^+$$

$$^{45}_{22}\text{Ti} \longrightarrow {}^{45}_{21}\text{Sc} + \beta^+$$

(iii) Electron Capture (EC):

A nucleus which is deficient in neutrons decays either by β^+ – decay or electron capture. In electron capture, a nucleus captures one of its own orbital electrons and emits a neutron. Because a K-shell electron (less often the L- shell) is captured in about 98 % of the events, this process is often called K-capture. The EC can be represented as

$$P + \bar{e} \longrightarrow n + \upsilon$$

In electron capture decay, the charge number of the decaying nucleus is reduced by one, its mass number remains the same. EC is represented by the generalized equation.

$$^{A}_{Z}X + \bar{e} \longrightarrow {}^{A}_{Z-1}Y + \upsilon$$

Both β^+ – decay and EC result in reducing the charge number of the decaying nucleus by one and shifting the daughter nucleus one place to the left in the periodic table. The difference lies in the fact that in the EC process as the name implies, an electron of the outer sphere of the same atom (K-shell) is captured by the nucleus leading to a transformation of proton into a neutron. The outer electrons, now one less in number, just balance the nuclear charge which is also one less now. No other change is involved following electron capture, except from the emission of X-rays which are produced by the rearrangement of outer electrons. The emission of X-rays is a characteristics of daughter nucleus.

Both these processes usually occur in the same nucleus. In some cases where sufficient energy (1.022 MeV) is not available for the creation of β^+ – particles, EC is the only process of decay. Decay by EC occurs as an alternative to all β^+ – decay, the converse is not true except under the conditions of resulting mass loss exceeding two electron masses. Examples of EC are given below:

$$^{55}_{26}Fe + \bar{e} \longrightarrow {}^{55}_{25}Mn + \upsilon$$

$$^{106}_{47}Ag + \bar{e} \longrightarrow {}^{106}_{46}Pd + \upsilon$$

$$^{37}_{18}Ar + \bar{e} \longrightarrow {}^{37}_{17}Cl + \upsilon$$

Some nuclides undergo both EC and positron emission.

$$^{22}_{11}Na + \bar{e} \longrightarrow {}^{22}_{10}Ne \ (3\%)$$

$$^{22}_{11}Na \longrightarrow {}^{22}_{10}Ne + \beta^+ \ (97\%)$$

3. Gamma Emission:

The emission of α – particles may leave the daughter nucleus in an excited state. This excited state usually loses this excited energy by the emission of short wavelength radiation called gamma radiation. This radiation has definite energy.

Since both the mass number and charge number of the de-exciting nucleus does not change. It is also known as *nuclear de-excitation*.

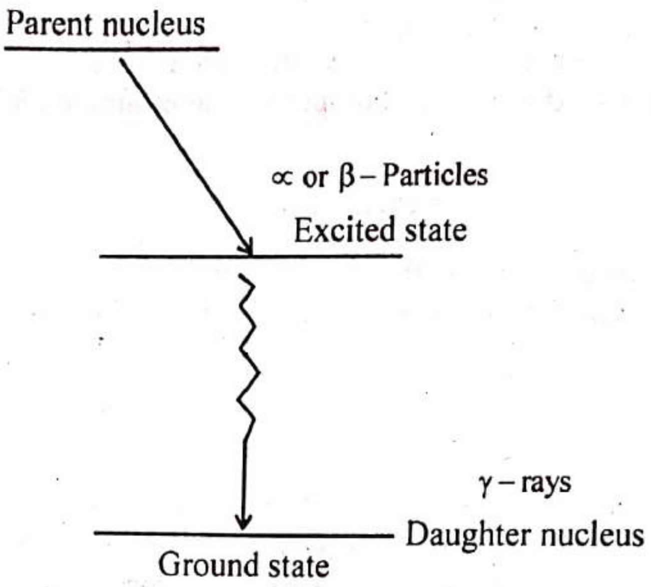


Fig. 7.10. Emission of γ – rays during a radioactive decay.

4. Internal Conversion (IC)

De-excitation can also occur by the method of internal conversion. This is possible when two levels have the same total angular momentum and when gamma transition between them is forbidden. Under such conditions the excited nucleus may interact with an orbital electron in such a way that the excitation energy is transformed to the orbital electron, which is then emitted. This type of electron conversion is called *internal conversion* (IC). Electrons from the IC are mono-energetic (have same energy) and thus differ from electrons of β – decay (which usually have energy from zero to maximum). This is possible as the wave function of the electron is not zero inside the nucleus. If the energy, of conversion electron exceeds the binding energy. E_B of the orbital electron, the electron is ejected with a kinetic energy, Ee,

$$E_e = (E_i - E_f) - E_B$$

or $$E_e = E_\gamma - E_B \quad (7.6)$$

Where E_γ is the gamma transition energy being the excess energy of the initial and the final energy. Since the K-shell electrons are closest to the nucleus, these are usually involved in internal conversion. The conversion electrons produce a series of mono energetic lines, and not a continuous spectrum as in β – emission.

5. Isomeric Transition (IT)

Nuclides having excited levels but do not decay instantaneously are called isomeric nuclei. The various excited levels are called isomeric levels. They decay either by gamma emission or by internal conversion. The transition leading to the de-excitation of such levels is called *isomeric transition* (IT). The decay of ^{60}Co by isomeric transition is shown below. The half-life of isomeric level is 10.6 min.

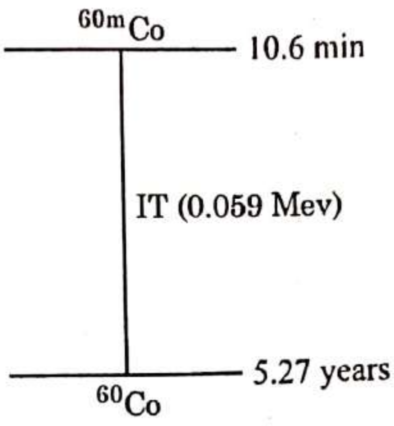


Fig. 7.11. Decay scheme by IT of $^{60m}C_o$

7.16 KINETICS OF RADIOACTIVE DECAY

Radioactive nuclei decay by first order kinetics. The rate of radioactive decay does not depend on the physical or chemical state of the sample. Since radioactivity is a nuclear phenomenon, a radioactive nuclide will emit the same type of radiation at the same rate, regardless of its chemical composition, its temperature, applied pressure or the presence of electrostatic or magnetic fields. The rate of decay at any instant of time is proportional to the number of radioactive atoms present.

$$-\frac{dN}{dt} \propto N$$

or $$-\frac{dN}{dt} = \lambda N$$

Where N is the number of atoms remaining at any time t. λ (lambda) is a proportionality constant called the decay constant and is characteristics of the given element. It represents the fraction of total number of atoms of radioactive element transformed per unit time, and is often expressed in reciprocal second (s^{-1}).

The above equation can be written as

$$-\frac{dN}{N} = \lambda dt \qquad (7.8)$$

On integrating Eq. 7.8 we get

$$\int\frac{dN}{N} = -\lambda \int dt$$

$$\text{In } N = -\lambda t + Z \qquad (7.9)$$

Where Z is constant of integration. When t = 0, then N = No, where No represents the initial number of atoms. So

$$Z = \text{ln } N_o \qquad (7.10)$$

Substituting value of Z into Eq. 7.9, we have

$$\text{In } N = -\lambda t + \text{In } N_o$$

or $\ln N - \ln N_0 = -\lambda t$

or $\ln \frac{N}{N_0} = -\lambda t$

or $\ln \frac{N_0}{N} = \lambda t$

or $\lambda = \frac{1}{t} \ln \frac{N_0}{N}$

or $\lambda = \frac{2.303}{t} \log \frac{N_0}{N}$ (7.11)

Equation 7.11 is the required kinetio expression for radioactive decay and is identical with the first order kinetic equation. Equation (7.11) can be written in the exponential form as

∴ $\ln \frac{N}{N_0} = -\lambda t$

or $\frac{N}{N_0} = e^{-\lambda t}$

or $N = N_0 e^{-\lambda t}$ (7.12)

Equation (7.12) represents the exponential form of the decay law.

Example 7.5. A radioactive element decays with a decay constant of 2.0×10^{-4} s^{-1}. How long will it take for 0.50 g of the substance to decay to 0.10 g?

Solution

$\lambda = 2.0 \times 10^{-4} s^{-1}$

$N_0 = 0.50g$

$N = 0.10g$

On applying Eq. 7.11

$\lambda = \frac{2.303}{t} \log \frac{N_0}{N}$

or $t = \frac{2.303}{\lambda} \log \frac{N_0}{N}$

or $t = \frac{2.303}{2.0 \times 10^{-4}} \log \frac{0.50}{0.10} = 8047.15$ seconds.

7.17 HALF-LIFE AND DECAY CONSTANT

According to law of radioactive disintegration, the proportion of atoms disintegrating is constant for any given period of time. This means that a certain fraction of the atoms, one third, for example, would decay in a given period of time. For convenience, the time required for one half of the atoms to decay is frequently designated. This is called the half life. It is defined as the time in which the radioactive atoms are reduced to half of their initial amount.

It is equal to the time required to reduce the activity of a radioactive element to half of the initial value.

It is the time required for the disintegration rate to decrease by 50%.

A radioactive substance emits α, β or $\gamma -$rays during its decay. The radioactive decay is a random process and one could not predict which atom will decay next or which particular atom will decay. It may decay immediately or it may not decay for million of years. Therefore, if we are dealing with one atom of a radioactive element, we cannot tell how old it is. Since we cannot talk about one atom we can talk only group of atoms. the larger the group, the more accurate will be the results. We take a known number of radioactive atoms (say, 20,000) and wait till such time that half of these (10,000) have decayed into daughter elements. This time is called the half-life time of that particular radioactive element.

Half-life period is a measure of the radioactivity of the element, shorter the half-life period of a radioactive substance, the longer the number of atoms that are disintegrating in unit time. It is denoted by $t_{1/2}$. Its relation to decay constant (λ) is given as.

According to decay laws

$$\lambda = \frac{2.303}{t} \log \frac{N_0}{N}$$

when $t = t_{1/2}$, then $N = N_0/2$

$$t_{1/2} = \frac{2.303}{\lambda} \log {}^{N_0}\!/_{N_0/2}$$

or $$t_{1/2} = \frac{2.303}{\lambda} \log 2$$

or $$t_{1/2} = \frac{0.693}{\lambda} \qquad (7.13)$$

Equation (7.13) shows that the time necessary for half of the quantity of a radioactive element to disintegrate, is constant, independent of the initial amount present and characteristics of the given radioactive element. Half-life is a useful property for the identification of various radioactive species. Thus if half-life period of a radioactive element is known, its decay constant can be calculated and vice versa. The half-life periods of different radioactive elements vary widely ranging from a fraction of second to millions of years.

Table 7.5 Half lives of some radioactive elements.

Isotope	$t_{1/2}$
$^{214}_{85}At$	1×10^{-6} seconds
$^{212}_{84}Po$	3×10^{-7} seconds
$^{214}_{83}Bi$	19.7 minutes
$^{210}_{82}Pb$	19.7 years
$^{238}_{92}U$	4.5×10^{9} years
$^{232}_{90}Th$	1.3×10^{10} years

Determination of Half-life and Decay constant

Half-life ($t_{1/2}$) and decay constant (λ) are characteristics of a given radioactive element. Since λ is a constant, hence life period of a particular radioactive element is independent of the amount of radioactive element or its initial concentration. It must be kept in mind that no sample of a radioactive element can ever decay completely, converting all the nuclei into daughter elements. This is because in any half-life period only one-half of the existing nuclei decay. In other words, it will take infinite time for the entire sample to decay.

Half-life of a radioactive element can be determined by observing its rate of decay. The rate of decay or activity of a radioactive element is proportional to the number of atoms present at that time;

$$-\frac{dN}{dt} = A = \lambda N$$

If we determine the number of atoms decaying per unit time (A) of a given sample of radioactive substance experimentally and plot a graph between log A and time, a straight line plot is obtained, as shown in fig. 7.12.

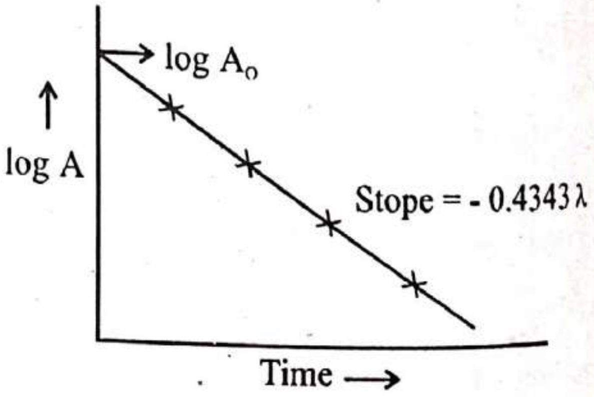


Fig. 7.12. Radioactive decay curve on a semi-log paper

According to decay law

$$2.303 \log\left(\frac{N}{N_0}\right) = -\lambda t$$

or $$2.303 \log\left(\frac{A}{A_0}\right) = -\lambda t$$

or $$\log\left(\frac{A}{A_0}\right) = -\frac{\lambda t}{2.303}$$

or $$\left(\frac{A}{A_O}\right) = -0.4343\ \lambda t$$

or $$\log A = \log A_0 - 0.4343\ \lambda t \qquad (7.14)$$

Equation (7.14) is an equation of straight like of the type y = mx + c. The slope of this line will be -0.1313λ. By knowing λ, the $t_{1/2}$ can be calculated.

$$t_{1/2} = \frac{0.693}{\lambda}$$

Example: 7.7. The half-life of radium is 1590 years. How long will it take for a sample of radium to decay to 10% of its original radioactivity?

Solution:

$$t½ = 1590 \text{ years.}$$

Let $N_O = a,\ N = \frac{a}{10}$

$$\lambda = \frac{0.693}{t_{1/2}}$$

$$\lambda = \frac{0.693}{1590} = 4.36 \times 10^{-4}\ \text{years}^{-1}$$

$$t = \frac{1}{\lambda}\ \text{In}\ \frac{N_0}{N}$$

$$= \frac{1}{4.36 \times 10^{-4}}\ \text{In}\ \frac{a}{a/10} = 5280 \text{ years.}$$

After 5280 years 10% of the original radioactivity remains.

$$N_o = 1,\ N = (1\text{-}0.01) = 0.99\text{g},\ t = 50 \text{ seconds}$$

Thus $\lambda = \frac{1}{t}\ \text{In}\ \frac{N_0}{N}$

or $$\lambda = \frac{1}{50}\ \text{In}\ \frac{1}{0.99} = 2.02 \times 10^{-4}\ s^{-1}$$

$$\text{Half-life} = \frac{0.963}{\lambda} = \frac{0.963}{2.02 \times 10^{-4}}\ 3240 \text{ sec onds}$$

Example 7.8. If a radioactive substance loses 95% of its activity in 110 minutes, what is its half-life?

Solution

$$t = 110 \text{ minutes}$$

Let $N_O = 100$, then $N = 100 - 95 = 5$

$$\lambda = \frac{1}{t} \ln \frac{N_O}{N}$$

or
$$\lambda = \frac{1}{110} \ln \frac{100}{5} = 0.02718 \text{ min}^{-1}$$

$$t_{1/2} = \frac{0.963}{\lambda} = \frac{0.693}{0.02718} = 25.44 \text{ minutes}$$

7.18 AVERAGE OR MEAN LIFE

According to decay law the rate of decay is proportional to the number of atoms of a particular element present. As disintegration proceeds in a given sample, the number of its atoms goes on decreasing. This process of disintegration will, therefore continue for an indefinite period. Total decay period of an element is therefore infinity. Use of total decay period for radioelements would thus be meaningless. Thus to differentiate between the radioactive elements, we define a quantity known as average or mean life instead of total decay period or life period, mean life is reciprocal of the decay constant (λ). It is represented by τ.

Theoretically the average life of a radioactive element is found by multiplying every possible life period "t" from zero to infinity by the number of atoms having that expectation of life and then dividing by the total number of atoms present at the beginning.

or

The average life period of a particular radioactive element is found by sum of the times of existence of all the atoms divided by their initial number. If N is very large, then sum may be approximated to an equivalent integral. Thus

$$\tau = -\int_0^\infty \frac{t.dN}{N_0} \qquad (7.15)$$

According to decay law

$$-\frac{dN}{dt} = \lambda N$$

$$-dN = \lambda N.\, dt \qquad (7.16)$$

Since dN atoms decay in time dt, therefore the life time of these atoms lies between t and dt. As dt is very small interval of time we may assume that these atoms have lived for time 't'. Hence the half life time of these atoms is equal to t-dN. By substituting Eq. (7.16) into 7.15, we get

$$\tau = \frac{1}{N_o}\int_0^\infty t\lambda N\,dt$$

$$\tau = \frac{1}{N_o}\int_0^\infty t\lambda N_o e^{-\lambda t}.dt \qquad \therefore\; N = N_0 e^{-\lambda t}$$

$$\tau = \int_0^\infty t\,\lambda e^{-\lambda t}dt$$

$$\tau = \lambda\int_0^\infty t.e^{-\lambda t}dt \qquad \therefore\; \lambda \text{ is constant} \qquad (7.17)$$

Equation (7.17) can be solved by integration by parts

$$\int u dv = uv - \int v du \qquad (7.18)$$

Let t = u so that dt = du and $e^{-\lambda t}\,dt = dv$

Which gives $v = -\frac{e^{-\lambda t}}{\lambda}$ $\qquad \therefore\; \int dv = \int e^{-\lambda t}dt = -\frac{e^{-\lambda t}}{\lambda}$

$$\tau = \lambda\left[\left[\frac{t.e^{-\lambda t}}{-\lambda}\right]_0^\infty - \int_0^\infty \frac{e^{-\lambda t}}{-\lambda}.dt\right]$$

$$\tau = \lambda\left[\left[\frac{t.e^{-\lambda t}}{-\lambda}\right]_0^\infty + \frac{1}{\lambda}\int_0^\infty e^{-\lambda t}.dt\right]$$

$$\tau = \lambda\left[\frac{t.e^{-\lambda t}}{-\lambda}\right]_0^\infty + \frac{\lambda}{\lambda}\left[\frac{e^{-\lambda t}}{-\lambda}\right]_0^\infty$$

$$\tau = \left[-te^{-\lambda t}\right]_0^\infty + \left[\frac{e^{-\lambda t}}{-\lambda}\right]_0^\infty$$

$$\tau = -\propto e^{-\lambda\infty} - (-)0 - \frac{1}{\lambda}\left[e^{-\lambda\infty} - e^{-\lambda(o)}\right]$$

$$\tau = -\frac{-\infty}{e^{\lambda\infty}} + 0 - \frac{1}{\lambda}\left[\frac{1}{e^{\lambda\infty}} - \frac{1}{e^{o}}\right]$$

$$\tau = 0 + 0 - \frac{1}{\lambda}\left[0 - 1\right]$$

$$\tau = \frac{1}{\lambda}$$

$$\tau = \frac{t_{1/2}}{0.693}$$

or $$\tau = 1.443 \times t_{1/2}$$

$$\therefore \quad e^{\infty} = \infty$$

$$\frac{1}{\infty} = 0$$

$$e^{o} = 1$$

In is obvious from Eq (7.20) that mean life is greater than the half life by a factor of 1.443. The mean life can be easily calculated if half-life is known.

7.19 THEORY OF RADIOACTIVE DISINTEGRATION

Rutherford and Soddy (1903) postulated a theory of radioactive disintegration. According to their theory nuclei of radioactive elements are unstable and decompose spontaneously by emission of an α or β particle to form a new element of different chemical and physical properties. The α and $\beta-$particles are ejected out of the nucleus undergoing disintegrating process. The $\gamma-$radiation arises from energy rearrangements within the nucleus after an α or $\beta-$particle ejection. The rearrangement leads to a lower potential energy, the excess is evolved as a quantum of energy of the frequency of $\gamma-$rays. Not all nuclear transformations are accompanied by emission of $\gamma-$rays. We can also say that the $\gamma-$rays are the secondary effects of nuclear disintegration process.

For example, when uranium 1 with A = 238 and Z = 92 emits an α particle to yield uranium X_1, the mass should decrease by four units to A = 234 and the nuclear charge by 2 units to Z = 90. Since the nuclear charge has decreased, two external electrons which are no longer necessary will also be lost and we obtain a new element of A = 234 and Z = 90, which is an isotope of thorium.

$$U_I \longrightarrow UX_I + \alpha$$

$$_{92}U^{238} \longrightarrow {}_{90}Th^{234} + {}_{2}\alpha^{4}$$

$$4.49 \times 10^{9}\,y \qquad 24.1\ d$$

Again when uranium X_1 emits a β particle, the nuclear mass remains unchanged, but the nuclear charge increased to Z = 91, the new product uranium X_2, has now a mass of 234 and atomic no. of 91 and hence is an isotope of protactinium.

$$UX_I \longrightarrow UX_2 + \beta^-$$

or $$_{90}Th^{234} \longrightarrow {}_{91}Pa^{234} + \beta^-$$

$$(24.1\ d) \qquad (1.18\ m)$$

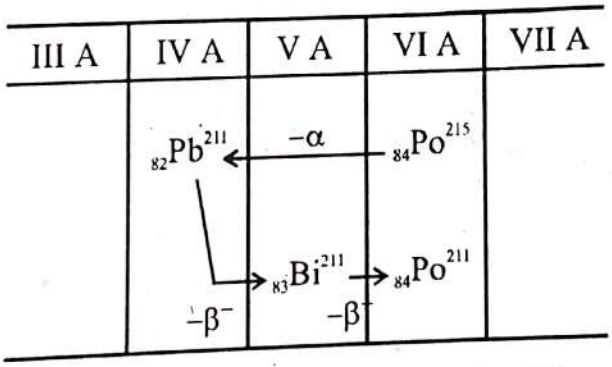
This idea, that as a result of radioactive spontaneous disintegration new elements are formed, has been amply (on large scale) verified, and is a well established principle or fact in the field of radioactivity.

The transformation brought about by the emission of an α or β particle from the nucleus is summarized in the **Fajans-Sodyd-Russelt displacement law**. This law states that whenever a parent nucleus emits an α – particle, its atomic number is decreased by two units and the new element is shifted two positions to the left in the periodic table from that of the parent. On the other hand, when the parent nucleus emits a β – particle the atomic number is increased by one, and hence the product is shifted one place to the right in the periodic table. The following example will illustrate the law.

(i) Polonium ($_{84}Po^{215}$) is in group VIA of the periodic table. On losing an α – particle, it is transformed into radioactive lead ($_{82}Pb^{211}$), which belongs to IVA group, i.e, two places to the left of parent element.

(ii) Radioactive lead ($_{82}Pb^{211}$) emits a β – particle, resulting in the formation of radioactive bismith ($_{83}Bi^{211}$), which belongs to group VA, i.e., one place to the right of parent element.

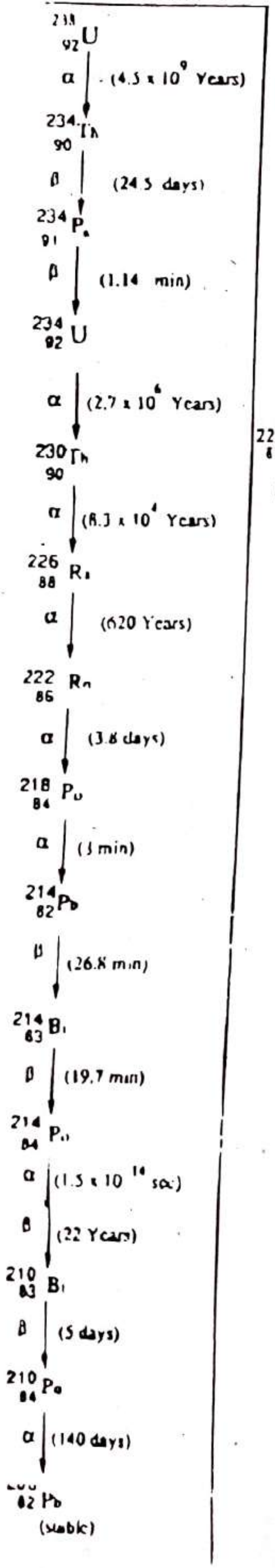
(iii) Radioactive bismith emits a β – particle, resulting in the formation of $_{84}Po^{211}$, which belong to group VIA, i.e., one place to the right of the parent nucleus. There examples are summarized in the following table.



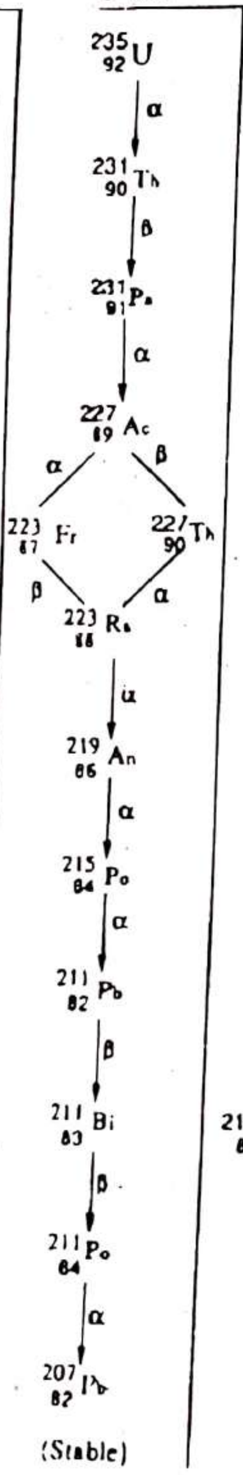
Here $_{84}Po^{215}$, and $_{84}Po^{211}$ are isotopes, while $_{82}Pb^{211}$, $_{83}Bi^{211}$ and $_{84}Po^{211}$ are isobars. *From this we conclude that a β – particle emission results in the formation of an isobar while an isotope is produced as a result of the combined emission of one alpha and two beta particles.* Radioactive elements may undergo successive disintegrations to give a chain of species known as radioactive decay series. There are three different series of naturally occurring radioactive elements. There is a fourth series for the artificially produced radioactive elements.

(i)	The uranium series	Natural
(ii)	The Actinium series	
(iii)	The Thorium series	
(iv)	The Naptunium series	Artificial

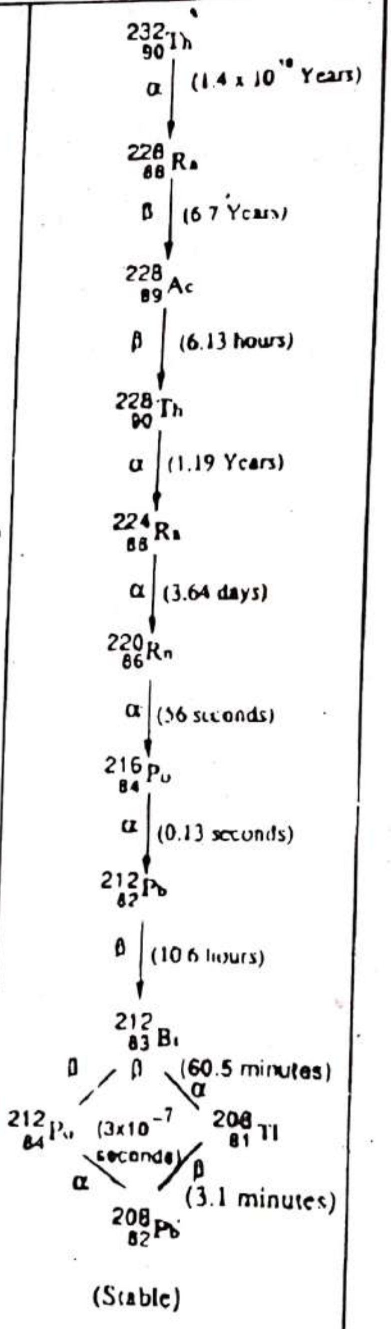
The Uranium Series ($t_{1/2}$)



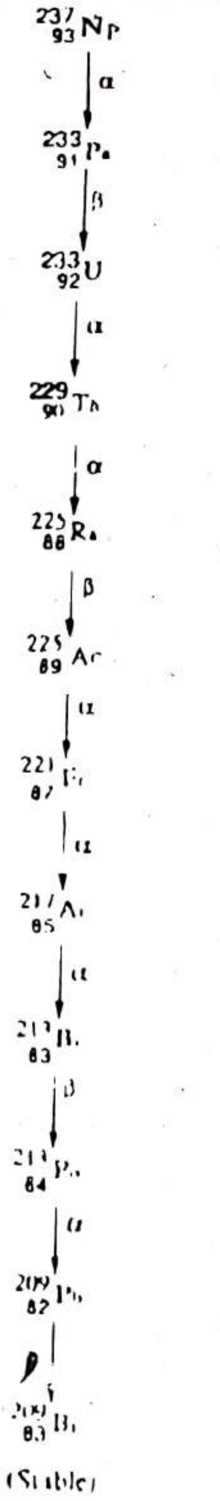
The Actinium Series



The Thorium Series ($t_{1/2}$)



The Neptunium Series



From these series, it may be noted that expulsion of an $\alpha-$particle and subsequent expulsion of two $\beta-$particles brings the element back to the same position in the periodic table. i.e., isotopes are formed.

7.20 ARTIFICIAL OR INDUCED RADIOACTIVITY

We know that some radioelements such as uranium, thorium, radium etc are found in nature. They are called natural radioactive elements and their radioactivity is called as natural radioactivity. The naturally occurring radioactive substances were the only available for study until 1934. In January of that year Irene Curie (daughter of Merri Curie) and F-Joliot discovered that it is possible to make a radioactive isotopes of several elements by suitable nuclear reactions. They studied the effect of bombarding light elements as boron aluminium and magnesium with high energy $\alpha-$particles from polonium. This very important discovery of artificial radioactivity came in the course of their experiments on the production of positions by bombardment of these elements with $\alpha-$particles. The Curie-Joliot discovery was that the boron and aluminum targets continue to emit positron after removal of the $\alpha-$source and that the induced radioactivity in each case decayed with a characteristic half-life.

Much earlier, in 1919, Rutherford had produced nuclear transmutations by $\alpha-$particle, bombardment and the new phenomenon of induced radioactivity was quickly understood in terms of the production of new, unstable nuclei. From B, the unstable nucleus N^{13} is produced (the stable nitrogen nuclei are N^{14}, N^{15}) from Al, the product is P^{30} (the only stable phosphorus is P^{31}).

At the time that artificial radioactivity was discovered, several laboratories had developed and put into operation devices for the acceleration of hydrogen ion and helium ions to energies at which nuclear transmutations were produced. In addition, the discovery of neutrons by J. Chadwick in 1932 and the chemical concentration of deuterium by G.N. Lewis and R.T. Macdonald in 1933 made available two additional bombarding particles which turned out to be especially useful for the production of induced activities.

Since that time, many such elements have been observed, and it has been found that, the emissions may involve not only positrons, but electrons and $\gamma-$radiations. Since this type of radioactivity does not arise spontaneously, but must be brought about by preliminary appropriate bombardment, the phenomenon is referred to as artificial or induced radioactivity.

or

The phenomenon of converting an atom into a radioactive atom by bombarding it with a fast moving particles is known as artificial radioactivity. This conversion of one element into another is called *transmutation* of an element.

It must be noted that artificial radioactivity is just like the natural radioactivity, since it obeys the same laws. Hence, the term artificial radioactivity refers to the way in which new radioactive substances are produced rather than to their decay.

In each instance the elements exhibiting induced radioactivity are unstable isotopes of the known elements. They do not appear among the stable isotopes, because their life-period is usually short, and hence it is hardly to be expected that they will be found in nature artificially radioactive elements behave very much like those which are naturally radioactive. They disintegrate in each instance according to the same rate law, and exhibit this constant half-life periods characteristic of the element in question. Further, although, some artificially radioactive elements may be produced by several different methods, once formed each element decomposes at the same rate and has thus the same life period. There is, however one aspect in which the two do differ. Whereas the natural radioactivity is confined only to the very massive nuclei; artificial radioactivity can be induced in light nuclei as well. Thus not only Bi^{210}, Pb^{209}, Pb^{205} and Au^{198} are artificially radioactive but also such light nuclei as H^3, He^6, Be^7 and C^{10}.

At least one radioactive isotope is now known for every element in the periodic table, and some elements have as many as 20 or more. The measured half-lives range from a small fraction of microsecond to many millions of years.

As a result of great deal of investigation, it has been found that artificial transmutations of the elements can be brought about by various projectiles e.g., α – particles neutrons, protons, electrons etc. and that proton is not necessarily one of the products. In nuclear reactions, a projectile particle is required and a light particle is produced in addition to the other product. A nuclear reaction is written as follows.

$$_7N^{14}(\propto,p)\ _8O^{17}$$

Signifying that $\propto$ - is the projectile and proton is the particle produced, where the nucleus bombarded is $_7N^{14}$ and the product is $_8O^{17}$.

Table 7.6 some artificially radioactive elements.

Element	Method of production	Half-life	Emitted Radiation
$_1H^3$	$_1H^2 + {}_1d^2$	12 year	e
$_5B^{12}$	$_5B^{11} + {}_1d^2$	0.022 sec	e
$_6C^{11}$	$_5B^{10} + {}_1d^2$	20.5 min	e^+
$_6C^{14}$	$_6C^{13} + {}_1d^2$	6000 years	e
$_7N^{13}$	$_6C^{12} + {}_1p^1$	10.1 min	e^+
$_8O^{15}$	$_7N^{14} + {}_1d^2$	2.1 min	e^+
$_{11}Na^{24}$	$_{11}Na^{23} + {}_1d^2$	14.8 hours	e
$_{15}P^{30}$	$_{13}Al^{27} + {}_2\propto^4$	2.55 min	e^+
$_{19}K^{38}$	$_{19}K^{39} + {}_0n^1$	7.5 min	e^+
$_{53}I^{124}$	$_{51}Sb^{121} + {}_2\propto^4$	4 days	e^+

7.21 SUCCESSIVE RADIOACTIVE DECAY AND RADIOACTIVE EQUILIBRIUM

The decay of a radioactive nucleus may result in the formation of a daughter nucleus which is also radioactive. The radioactive daughter in turn decays thus becoming parent to produce a new daughter nucleus which may be stable or radioactive. When such a radioactive sample is analyzed for its activity, the situation becomes complicated because of the further disintegration of the products. The rate of decay of the parent substance must represent the rate at which the product is formed. Since, the product itself disintegrates, and the rate of disintegration of this product increases with its accumulation, ultimately a stage is reached when the rate of formation of the product will be equal to the rate of disintegration of the product. The equilibrium thus obtained is called the *radioactive equilibrium*. This stage may be mathematically designated as,

$$\frac{dN_1}{dt} = \frac{dN_2}{dt} = \frac{dN_3}{dt} \tag{7.21}$$

Since for any substance $-dN/_{dt} = \lambda N$, therefore

$$\lambda_1 N_1 = \lambda_2 N_2 = \lambda_3 N_3$$

or $$\frac{N_1}{N_2} = \frac{\lambda_2}{\lambda_1} \qquad \therefore \lambda \alpha \frac{1}{t_{1/2}}$$

Hence $$\frac{\lambda_2}{\lambda_1} = \frac{(t_{1/2})_1}{(t_{1/2})_2} \text{ and } \frac{N_1}{N_2} = \frac{(t_{1/2})_1}{(t_{1/2})_2} \tag{7.22}$$

Hence at equilibrium, the various constituents of the system will be present in the ratio of their half-life periods. Thus the attainment of equilibrium depends on the average life periods of the radioelements involved. The shorter is the life, the more easily the equilibrium state is obtained. In any radioactive series, some elements can be found, which has very long life and hence attainment of equilibrium will take a very long time. The true equilibrium can be expected in minerals only. For examples in all U-minerals, the U : Ra ratio is found to be constant indicating thereby that the equilibrium exists in the sample, and also that the radium (Ra) is a disintegration product of the uranium.

Another characteristic of the radioactive equilibrium is that at equilibrium all the radioelements disintegrate at the same rate. For example, radium emits an α-particle and among its disintegration products, three other also emit α-particles. Since all of them disintegrate at the same rate at equilibrium, hence the no. of α-particles emitted by the sample will be four times than emitted by radium alone.

The radioactive equilibrium differs from chemical equilibrium in one respect viz. the radioactive equilibria are not reversible.

Let us take up the general case for the decay of a radioactive species 'A' to produce another radioactive species 'B' which further decays to 'C' which is stable.

$$A \xrightarrow{\lambda_1} B \xrightarrow{\lambda_2} C$$

λ_1 and λ_2 are the decay constants of A and B respectively. Let N_1 and N_2 represent the no. of atoms of A and B respectively present at time t and N_1^0 and N_2^0 be the number of A and B respectively at zero time, then

$$-\frac{dN_1}{dt} = \lambda_1 N_1 \tag{7.23}$$

Which on simplification gives

$$N_1 = N_1^0 \, e^{-\lambda_1 t} \tag{7.24}$$

Now the second species 'B' is formed at the rate at which the first decays, $\lambda_1 N_1$, and itself decays at the rate $\lambda_2 N_2$ thus the net rate of decay of 'B' is.

$$\frac{dN_2}{dt} = \lambda_1 N_1 - \lambda_2 N_2 \tag{7.25}$$

Putting the value of 'N_1' from (7.24) into (7.25) we get

$$\frac{dN_2}{dt} = \lambda_1 N_1^0 e^{-\lambda_1 t} - \lambda_2 N_2$$

$$\frac{dN_2}{dt} + \lambda_2 N_2 = \lambda_1 N_1^0 \, e^{-\lambda_1 t} \tag{7.26}$$

To make L.H.S of equation (7.26) exact differential, let us multiply this by $e^{\lambda_2 t}$

$$\left(\frac{dN_2}{dt} + \lambda_2 N_2\right) e^{\lambda_2 t} = \lambda_1 N_1^0 e^{-\lambda_1 t} \times e^{\lambda_2 t}$$

or $$e^{\lambda_2 t} \frac{dN_2}{dt} + N_2 \lambda_2 e^{\lambda_2 t} = \lambda_1 N_1^0 \, e^{-\lambda_1 t} \times e^{\lambda_2 t} \tag{7.27}$$

For this linear differential equation of first order we assume a solution of the form $N_2 = uv$, where u and v are functions of t, differentiating we obtain

$$\frac{d}{dt}(uv) = u.\frac{dv}{dt} + v.\frac{du}{dt}$$

$$\frac{d}{dt}\left(e^{\lambda_2 t}.N_2\right) = \lambda_1 N_1^0 \, e^{-\lambda_1 t}.\, e^{\lambda_2 t}$$

$$\frac{d}{dt}\left(e^{\lambda_2 t}.N_2\right) = \lambda_1 N_1^0 \, e^{(\lambda_2 - \lambda_1)t}$$

$$\int d(e^{\lambda_2 t}.N_2) = \int \lambda_1 N_1^0 \, e^{(\lambda_2 - \lambda_1)t}.dt$$ on integration we get

$$e^{\lambda_2 t}.N_2 = \frac{\lambda_1 N_1^0}{\lambda_2 - \lambda_1} e^{(\lambda_2 - \lambda_1)t} + C \tag{7.28}$$

Where C is constant of integration which can be evaluated by applying the initial conditions that when t = 0, then $N_2 = 0$

$$0 = \frac{\lambda_1 N_1^0}{\lambda_2 - \lambda_1} e^o + C \qquad \therefore e^o = 1$$

$$C = -\frac{\lambda_1 N_1^0}{\lambda_2 - \lambda_1}$$

Putting the value of C into 7.28 we get

$$e^{\lambda_2 t}.N_2 = \frac{\lambda_1 N_1^0}{\lambda_2 - \lambda_1} e^{(\lambda_2 - \lambda_1)t} - \frac{\lambda_1 N_1^0}{\lambda_2 - \lambda_1} \tag{7.29}$$

Dividing both sides of 7.29 by $e^{\lambda_2 t}$

$$N_2 = \frac{\lambda_1 N_1^0}{\lambda_2 - \lambda_1} e^{-\lambda_1 t} - \frac{\lambda_1 N_1^0}{\lambda_2 - \lambda_1} e^{-\lambda_2 t}$$

or

$$N_2 = \frac{\lambda_1 N_1^0}{\lambda_2 - \lambda_1} \left(e^{-\lambda_1 t} - e^{-\lambda_2 t}\right)$$

$$N_2 = \frac{\lambda_1}{\lambda_2 - \lambda_1} N_1^0 \left(e^{-\lambda_1 t} - e^{-\lambda_2 t}\right) \tag{7.30}$$

In applying equation 7.30 to considerations of radioactive (parent and daughter) pairs, we can distinguish two general cases, depending on which of the two substances has the longer half-life.

(i) Transient Equilibrium:

If the half-life of the parent element is greater (but not very large) than that of the daughter element by a small factor (about 10) rather than a large factor (10^4 or more), the state of so called radioactive equilibrium is called transient equilibrium. At this stage, the ratio of the disintegration rates of parent and daughter become constant i.e.,

$$\frac{1}{\lambda_1} > \frac{1}{\lambda_2} \text{ or } \lambda_1 < \lambda_2 \text{ or } \lambda_2 > \lambda_1$$

It means that when t becomes sufficiently large, $e^{-\lambda_2 t}$ is negligible compared with $e^{-\lambda_1 t}$, then

$$N_2 = \frac{\lambda_2}{\lambda_2 - \lambda_1} N_1^0 e^{-\lambda_1 t}$$

and since $N_1 = N_1^0 e^{-\lambda_1 t}$

$$N_2 = \frac{\lambda_1}{\lambda_2 - \lambda_1} N_1$$

$$\frac{N_2}{N_1} = \frac{\lambda_1}{\lambda_2 - \lambda_1}$$

or
$$\frac{N_1}{N_2} = \frac{\lambda_2 - \lambda_1}{\lambda_1}$$

or
$$N_1\lambda_1 = N_2\lambda_2 - N_2\lambda_1 \quad (7.31)$$

Since $\frac{N_2}{N_1}$ or $\frac{N_1}{N_2}$ is constant, therefore the above equations indicates a state of equilibrium; but the equilibrium is transient because N_1 and N_2 both decay at the decay rate of parent element. That is, in transient equilibrium also the daughter decays with the half-life of parent but its activity is larger than the parent.

(ii) Permanent or Secular Equilibrium:

If the decrease in the activity of the parent is insignificant during many half-lives of the daughter i.e., if the half-life of the parent is many times greater than the daughter or $\lambda_2 >>> \lambda_1$ then the equilibrium is called *permanent or secular equilibrium.*

or

A limiting case of radioactive equilibrium in which $\lambda_1 <<< \lambda_2$ and in which the parent activity does not decrease measurably during many daughter half-lives is known as secular equilibrium.

$$\frac{1}{\lambda_1} >> \frac{1}{\lambda_2}, \text{ then } \lambda_1 << \lambda_2 \text{ or } \lambda_2 >> \lambda_1$$

It means that after t becomes sufficiently very large, $e^{-\lambda_2 t}$ becomes negligible.

$$N_2 = \frac{\lambda_1}{\lambda_2 - \lambda_1} N_1^0 \, e^{-\lambda_1 t}$$

$$N_2 = \frac{\lambda_1}{\lambda_2} N_1^0 \, e^{-\lambda_1 t} \qquad \therefore \ \lambda_2 >> \lambda_1$$

$$N_2 = \frac{\lambda_1}{\lambda_2} N_1 \qquad \therefore \ N_1 = N_1^0 \, e^{-\lambda_1 t}$$

$$\frac{N_2}{N_1} = \frac{\lambda_1}{\lambda_2}$$

or
$$N_2\lambda_2 = N_1\lambda_1 \quad (7.32)$$

Equation 7.32 indicates a state of equilibrium in which no of atoms (N_1 and N_2) of two elements are inversely proportional to their decay constants. That is, in secular equilibrium, the activity of daughter will be equal to that of parent; and the daughter will decay with the half-life of the parent.

For the occurrence of secular equilibrium, the difference between the half-lives of parent and daughter is usually a factor of 10^4 or more. the decay of Ra^{226} with half life of 1620 years to Rn^{222} which has a half-life of only 3.8 days is a typical example in which secular equilibrium is attained.

(iii) No Equilibrium:

If the parent is shorter-lived than the daughter i.e., $\lambda_1 > \lambda_2$, no equilibrium is attained at any time. if one starts with pure parent, then as the parent decays, the amount of daughter will rise, passes through a maximum and finally decays with the characteristic half-life of the daughter.

7.22 NUCLEAR REACTIONS

Nuclear reaction is a process in which change in the character of a nucleus takes place either spontaneously or as a result of bombardment by a particle or a ray. A nuclear reaction takes place if a particle is able to enter a target nucleus. The particle which is used to strike a target nucleus is called a projectile.

The notation used for a nuclear reaction is analogous to that in chemical reaction, with reactants on the left and products on the right hand side of the equation. A nuclear reaction is generally represented by the following equation.

$$a + X \longrightarrow Y + b$$

Where X stands for target nucleus
a for projectile
Y for product nucleus
b for emitted particle or ray.

Table 7.7. Types of Nuclear Reactions

Type	Example	Representation
(p, γ)	$^{7}_{3}Li + ^{1}_{1}H \longrightarrow ^{8}_{4}Be + \gamma$	$^{7}_{3}Li\ (P,\gamma)\ ^{8}_{4}Be$
(p, n)	$^{7}_{3}Li + ^{1}_{1}H \longrightarrow ^{7}_{4}Be + ^{1}_{0}n$	$^{7}_{3}Li\ (P,n)\ ^{7}_{4}Be$
(p, α)	$^{7}_{3}Li + ^{1}_{1}H \longrightarrow ^{4}_{2}He + ^{4}_{2}He$	$^{7}_{3}Li\ (P,\alpha)\ ^{4}_{2}He$
(d, p)	$^{23}_{11}Na + ^{2}_{1}H \longrightarrow ^{24}_{11}Na + ^{1}_{1}H$	$^{23}_{11}Na\ (d,p)\ ^{24}_{11}Na$
(d, n)	$^{2}_{1}H + ^{2}_{1}H \longrightarrow ^{3}_{2}He + ^{1}_{0}n$	$^{2}_{1}H\ (d,n)\ ^{3}_{2}He$
(n, p)	$^{14}_{7}N + ^{1}_{0}n \longrightarrow ^{14}_{6}C + ^{1}_{1}H$	$^{14}_{7}N\ (n,p)\ ^{14}_{6}C$
(α, n)	$^{27}_{13}Al + ^{4}_{2}He \longrightarrow ^{30}_{16}P + ^{1}_{0}n$	$^{27}_{13}Al\ (\alpha,n)\ ^{30}_{15}P$
(α, p)	$^{14}_{7}N + ^{4}_{2}He \longrightarrow ^{17}_{8}O + ^{1}_{1}H$	$^{14}_{7}N\ (\alpha,p)\ ^{17}_{8}O$
(n, γ)	$^{59}_{27}Co + ^{1}_{0}n \longrightarrow ^{80}_{27}Co + \gamma$	$^{59}_{27}Co\ (n,\gamma)\ ^{60}_{27}Co$

A short hand notation is often used for the representation of nuclear reaction. This is known s Bethe's notation. According to this notation, the above reaction can be represented as

$$X\ (a,b)\ Y$$

Which implies that the particle 'a' comes in and particle 'b' goes out. the symbols 'a' and 'b' may stand for the neutron (n), alpha particle (α), deuteron (d), proton (p), and gamma ray (γ) etc. Some important types of nuclear reactions are shown in Table 7.7.

Comparison of Nuclear and Chemical Reactions

Nuclear reactions like chemical reactions are always accompanied by a release or absorption of energy and this is expressed by adding the them 'Q' to the right hand side of the equation. For example:

$$^{14}_{7}N + ^{4}_{2}He \longrightarrow ^{17}_{8}O + ^{1}_{1}H + Q$$

The quantity 'Q' is called the energy of reaction. Positive Q corresponds to energy release (exoergic reaction); negative 'Q' to energy absorption (endoergic reaction). Individual particles are involved in each case nucleons in nuclei and atoms is molecules respectively. Number of nucleons is conserved just as in chemical reactions, the number of atoms of each element is conserved. Moreover, law of conservation of energy applies to each. Some of the characteristics that differentiate between nuclear reactions and ordinary chemical reactions are summarized below:

Nuclear Reaction	Chemical Reaction
1. Elements may be converted from one to another.	No new elements can be produced.
2. Particles within the nucleus are involved.	Usually only outermost electrons are involved.
3. Often accompanied by release or absorption of tremendous amounts of energy.	Accompanied by release or absorption of relatively small amount of energy.
4. Rate of reaction is independent of factors such as concentration, temperature, pressure and catalyst etc.	Rate of reaction is influenced of external factors.
5. The quantities are defined per particle.	The quantities are defined per mole.
6. The quantity of matter is changed appreciably.	The quantity of matter is unchanged.
7. Nuclear reactions are very rare.	Chemical reactions are frequent.

7.23 NUCLEAR FISSION

Nuclear fission is a process in which a heavy nucleus is broken into two intermediate nuclei with the release of energy. This process is usually accompanied by the emission of neutrons.

E. Fermi (1934) studied the bombardment of uranium nucleus with slow neutrons and observed that the products show several different type of strong β-rays activity and some strong products of decay. At the same time O. Hahn and Strassman in Germany (1934-38) showed that when uranium (^{235}U) was irradiated with slow moving neutron, the product so formed has an atomic mass and atomic number considerably lower than that of uranium. It was shown that the products of the reaction were isotopes of barium and krypton.

Fission has been observed in some nuclides by neutrons, protons, electrons, helium ions and γ and X-rays of moderate energies and with higher bombarding energies (50 – 450 MeV) lighter elements such as Bi, Pb, Au Ta and some rare earths have been shown to undergo fission. By far the most important of these reactions is the neutron produced fission. The species ^{232}u, ^{235}U, ^{239}Pu ^{241}Au etc. undergo fission with thermal or with fast neutrons, whereas fission of ^{232}Th, ^{231}Pa and ^{238}U and other heavy nuclides require fast neutrons. Isotopes of some elements with atomic number above 80 are capable of undergoing fission. Some fissions are spontaneous, others require that the activation be supplied by bombardment. Nuclear fission is energetically favorable process for heavy atoms, since atoms with intermediate masses and greater binding energies per nucleon are formed.

It has been known from the work of Dempster with the mass spectrograph that ^{238}U possesses a rare isotope ^{235}U. Ordinary uranium is composed of 99.28 percent ^{238}U, 0.71 percent ^{235}U and ^{234}U about 0.01 percent. We can also say that there is approximately 1 atom of ^{235}U in every 143 atoms. Early in the study of fission the question arose as to which of isotopes of uranium underwent fission. The separation of very tiny samples of ^{238}U and ^{235}U by A.O. Nier made the first test possible and latter work proved that ^{238}U nuclei would undergo fission only when subjected to bombardment by fast neutrons. ^{235}U nuclei, on the other hand, would undergo fission by absorption of slow as well as fast neutrons. Apparently the energy of a slow neutron is sufficient to give the ^{235}U nucleus more than the activation energy, but it is not sufficient to give ^{238}U nucleus as much as its activation energy.

Consequently, slow neutrons would induce fission only in ^{233}U, ^{234}U, ^{235}U nuclei and fast neutrons would induce fission in ^{238}U as well as in ^{235}U. ^{233}U and ^{234}U are also isotopes of U).

The neutrons are the ideal nuclear bullets because unlike the heavy particles, they have no charge and so are not repelled by the target nucleus. When a slow neutron collides with ^{235}U nucleus, the new nucleus formed by the capture of neutron is unstable and splits up into two nuclei of medium atomic masses. One nucleus which is produced in the fission is barium (Z = 56) ,the other is krypton (Z = 36) plus a few addition neutrons and a tremendous amount of energy. The fission of U^{235} with slow neutron can be represented by the equation.

$$^{235}_{92}U + ^{1}_{0}n \longrightarrow ^{141}_{56}Ba + ^{92}_{36}Kr + 3\,^{1}_{0}n + Q$$

Where Q represents the energy released in the reaction.

Barium and krypton are not only fission products, other fragments are also produced. A given nucleus can split in many different ways, liberating enormous amounts of energy. Some of the possible fissions resulting from bombardment of fissionable ^{235}U with fast neutrons are shown below. The ^{236}U is a short lived intermediate.

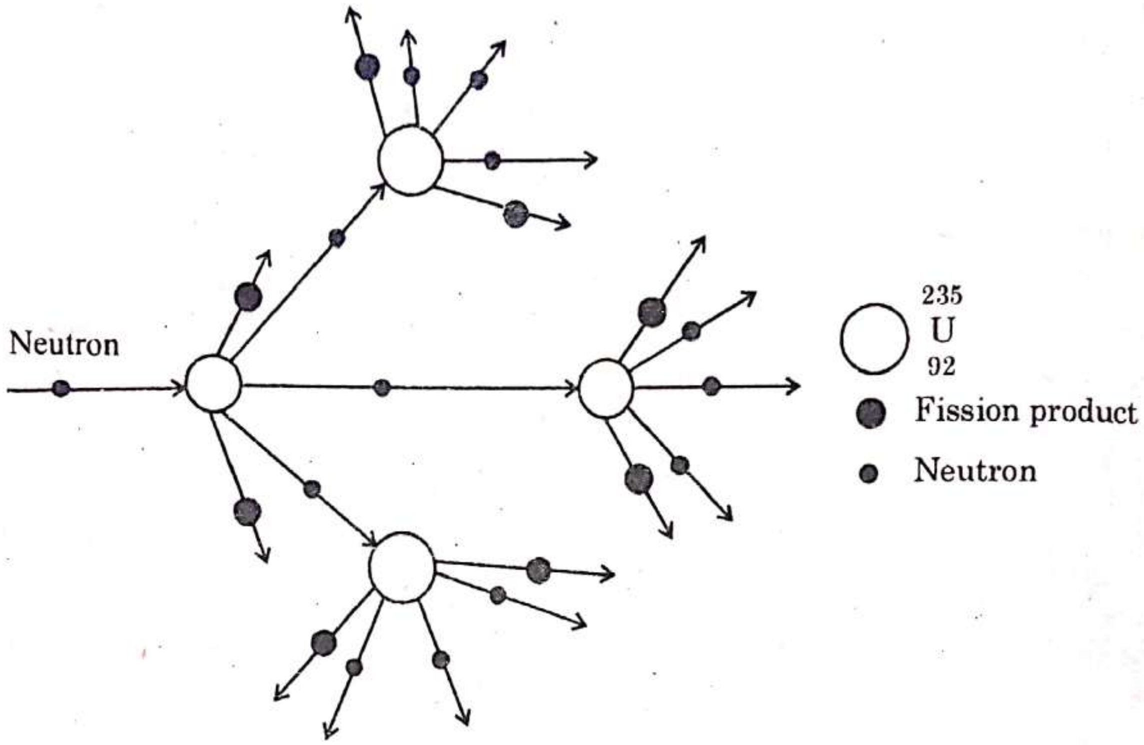


Fig 7.11 Fission Chain Reaction

It should be noted from the previous equation that the total mass number and total charge number are conserved on both sides of the equations. The fission fragments are radioactive and they decay in a number of steps into stable nuclei. The fission fragments contain too many neutrons for stability and therefore most of them decay by β emission. The three neutrons which are produced in fission of U^{235} are very useful is producing a *fission chain reaction*. Suppose we take a certain mass of uranium containing only atoms of ^{235}U and enclose it in a certain volume. Any stray slow neutron from cosmic ray or other sources will produce fission in one of the atoms of uranium. About three neutrons will be emitted in this fission. If the conditions are correct, these neutrons will produce fission in other uranium atoms. Hence a chain reaction will build up with explosive violence.

It is possible to arrange conditions such that only one neutron out of all the neutrons produced in one fission produces further fission. The remaining neutrons are allowed to escape or allowed to be captured by some other non fissionable atoms. The chain reaction will then proceed smoothly at its initial rate. The mass of the uranium required for producing a smooth chain reaction is called the *critical mass* and the volume occupied by the mass of uranium is called *critical volume*. In a nuclear reactor the fission chain reaction takes place at constant rate in a controlled manner. If the mass of uranium is less than the critical mass, the chain reaction will die. If, on the other hand, the mass is much larger than the critical mass the chain reaction will build up at a fast rate and an explosion will occur. This is the mechanism which is used in the nuclear bomb, usually called the atomic bomb/ atom bomb.

^{238}U can be made fissionable by converting it into ^{239}Pu through neutron bombardment. The following series of reactions then sets in:

$$^{238}_{92}U + {}_0n^1 \longrightarrow {}^{239}_{92}U + \gamma$$

$$^{239}_{92}U \longrightarrow {}^{239}_{93}Np + \beta^-$$

$$^{239}_{93}Np \longrightarrow {}^{239}_{94}Pu + \beta^-$$

i.e., the ^{238}U on capture of a neutron is transformed into ^{239}U, which is radioactive, and passes over with an emission of an electrons into transuranic element neptunium. This is also radioactive and emits an electron to form plutonium of atomic number 94. ^{239}Pu like ^{235}U undergoes fission.

Another fissionable isotope is $^{233}\underline{U}$ which can be obtained from ^{232}Th by irradiation with slow neutrons. The reactions involved are

$$^{232}_{90}Th + {}_0n^1 \longrightarrow {}^{233}_{90}Th$$

$$^{233}_{90}Th \longrightarrow {}^{233}_{91}Pa + \beta^-$$

$$^{233}_{91}Pa \longrightarrow {}^{233}_{92}U + \beta^-$$

7.24 THE ATOMIC BOMB

An atomic bomb is a device which releases an enormous amount of energy in a few seconds by nuclear fission. It works on the principle of fast neutron chains. A nuclear fuel (^{235}U or ^{239}Pu) is kept in sub critical segments in the bomb. These segments are forced into critical mass by using a conventional explosive, such as trinitrotoluene (TNT). Then neutrons released from the center of the bomb trigger chain fission leading to explosion. The large kinetic energy of the fission breaks building, the thermal energy burns the materials and the nuclear radiations harm living beings.

On 6th August 1945 an atomic bomb nicknamed "Little Boy" was dropped on Hiroshima, Japan, it contained ^{235}U fuel. On 9th August 1945 a bomb containing ^{239}Pu, nicknamed "Fat Man", was dropped on Negasaki, another Japanese town. These bombs extensively damaged the two towns and killed several thousands persons. In an actual explosion the temperature reached upto 10 million °C and pressure of several million atmosphere.

In fission weapons, a mass of fissile material (enriched uranium or plutonium) is assembled into a supercritical mass – the amount of material needed to start an exponentially growing nuclear chain reaction – either by shooting one piece of sub-critical material into another (the "gun" method) or by compressing a sub-critical sphere of material using chemical explosives to many times its original density (the "implosion" method). The latter approach is considered more sophisticated than the former and only the latter approach can be used if the fissile material is plutonium.

A major challenge in all nuclear weapon's design is to ensure that a significant fraction of the fuel is consumed before the weapon destroys itself. The amount of energy released by fission bombs can range from the equivalent of just under a ton of TNT, to upwards of 500,000 tons (500 kilotons) of TNT.

All fission reactions necessarily generate fission products, the radioactive remains of the atomic nuclei split by the fission reactions. Many fission products are either highly radioactive (but short-lived) or moderately radioactive (but long-lived), and as such are a serious form of radioactive contamination if not fully contained. Fission products are the principal radioactive component of nuclear fallout.

The most commonly used fissile materials for nuclear weapons applications have been **uranium-235** and **plutonium-239**. less commonly used has been **uranium-233**. **Neuptunium-237** and some isotopes of **americium** may be usable for nuclear explosives as well, but it is not clear that this has ever been implemented, and even their plausible use in nuclear weapons is a matter of scientific dispute.

7.25 NUCLEAR FUSION AND STELLAR ENERGY

Nuclear fusion may be considered as the reverse of fission. It may be defined as the process of combining two lighter nuclei to form a heavier nucleus with the release of energy. It has been observed that tremendous amount of energy is obtained when lighter nuclei such as hydrogen, deuterium and helium are fused to form heavier nuclei. Such reactions are also known as thermonuclear reactions, as these reactions occur at high temperature. Some examples of nuclear reactions are:

$$^{2}_{1}H + ^{2}_{1}H \longrightarrow ^{3}_{2}He + ^{1}_{0}n + 3.27MeV$$

or $$^{2}_{1}H + ^{2}_{1}H \longrightarrow ^{3}_{1}H + ^{1}_{1}H + 4.03MeV$$

$$^{2}_{1}H + ^{3}_{1}H \longrightarrow ^{4}_{2}He + ^{1}_{0}n + 17.6MeV$$

$$^{2}_{1}H + ^{3}_{2}He \longrightarrow ^{4}_{2}He + ^{1}_{1}H + 1.8MeV$$

The fusion of two deuteron nuclei is known as d-d reaction. It will be noted that both $^{3}_{1}H$ and $^{3}_{2}He$ are products of deuteron-deuteron reactions. Each of these reactions can be produced in a suitable particle accelerator.

The history of fusion research is quite different from that of fission research. With fission the reactor came first, and then bomb was built. With fusion, the bomb was built long before any progress was made toward the construction of a controlled fusion reactor. More than 40 years after the first hydrogen bomb was exploded, the feasibility of controlled fusion reactions is still open to debate. The reaction that is most likely to fuel the first fusion reactor is the thermonuclear d-t or deuterium-tritium reaction.

$$^{2}_{1}H + ^{3}_{1}H \longrightarrow ^{4}_{2}He + ^{1}_{0}n$$

Each fusion reaction is characterized by a specific ignition temperature which must be surpassed before the reaction can occur. The d-t reaction has an ignition temperature above 10^{8} K. Any substance at temperature above 10^{8}K will exist as a completely ionized gas or plasma. The goals of fusion research include:

1. To achieve the required temperature to ignite the fusion reaction.
2. To keep the plasma together at this temperature long enough to get useful amounts of energy.
3. To obtain more energy from thermonuclear reaction than is used to heat the plasma to the ignition temperature.

Thermonuclear fusion reactions are very probable in sun and stars, the temperatures of which are very high. Bethe (1939) developed the theory for the production of stellar energy in which protons by suitable reactions, are transmuted into helium nuclei, thereby releasing, energy which is transformed into radiation. One possible series of reactions in which protons are converted into helium nuclei is one in which carbon and nitrogen act as catalyst. This series is usually referred to as the carbon nitrogen cycle and consists of the following reactions.

$${}^{12}_{6}C + {}^{1}_{1}H \longrightarrow {}^{13}_{7}N + \gamma$$

$${}^{13}_{7}N \longrightarrow {}^{13}_{6}C + \beta^{+} + \nu$$

$${}^{13}_{6}C + {}^{1}_{1}H \longrightarrow {}^{14}_{7}N + \gamma$$

$${}^{14}_{7}N + {}^{1}_{1}H \longrightarrow {}^{15}_{8}O + \gamma$$

The energy released by this cycle is 26.7 MeV.

$${}^{15}_{8}O \longrightarrow {}^{15}_{7}N + \beta^{+} + \nu$$

$${}^{15}_{7}N + {}^{1}_{1}H \longrightarrow {}^{12}_{6}C + {}^{4}_{2}He + \gamma$$

Attempts to produce controlled thermonuclear fusion reactions have so far been unsuccessful.

Difference between Nuclear Fission and Fusion

Nuclear Fission	Nuclear Fusion
1. The process occurs only in the nuclei of heavy elements.	The process occurs in the nuclei of light elements.
2. The process involves the fission of heavy nucleus to the lighter nuclei.	The process involves the fusion of the lighter nuclei to a heavy nucleus.
3. The process take place at ordinary temperature.	The process takes place at high temperature (10^8K)
4. The energy liberated during the process is high (200 MeV per fission).	The energy liberated during the process is comparatively low (3-24 MeV per fusion).
5. The process can be controlled for useful purposes.	The process can not be controlled.
6. Atom bomb is based on the principle of nuclear fission.	Hydrogen bomb is based on the principle of nuclear fusion.

Nuclear Fission	Nuclear Fusion
7. Percentage efficiency of energy conversion is comparatively less.	Percentage efficiency of energy conversion is high (four times to that of fission process).
8. Lesser amount of energy per unit mass of reacting atoms is produced.	Much larger amount of energy per unit mass of reacting atoms is produced.
9. Fission products are radioactive and dangerous.	Fusion products are not dangerous.
10. Fuel can be stored in fission.	Fuel cannot be stored.
11. Solid or liquid fuel is used.	Fuel is in the plasma state.

7.26 HYDROGEN BOMB

The hydrogen bomb is about 1000 times more powerful than the atom bomb. The mechanism of this bomb lies in the fusion of hydrogen or other lighter nuclei to produce heavy nuclei and releasing an enormous amount of energy. The working of hydrogen bomb is essentially dependent on two conditions-extremely high temperature and pressure. The hydrogen bomb is superior to atomic bomb in that it has no limitation of critical size. In an atomic bomb whenever the mass of active material exceeds the critical mass, there is spontaneous explosion, whereas in hydrogen bomb the explosion does not occur till the active material is brought to ignition temperature, however, great mass of active material is used.

Hydrogen bomb was first exploded in November 1952 in Marshall Island. After about 8 months of this. Russians also exploded a thermonuclear bombs which was about 1 million ton more powerful than TNT. Deuterium and tritium were used in both these bombs. The operation of hydrogen involves the sudden release of enormous amount of energy by nuclear fusion. The heat and kinetic energy released in fusion destroys the place where such a bomb is exploded. The temperature required for fusion is this bomb is initially produced by a nuclear fission. The fission reactions function as a fuse to produce a temperature sufficient to start the fusion reaction. Because of the tremendous heat produce in H-bomb, it is called a *thermonuclear bomb.*

The actual reaction used in H-bomb is a secret. Such possible fusion reactions involved in such bombs are as follows:

$$^{2}_{1}H + ^{3}_{1}H \longrightarrow ^{4}_{2}He + ^{1}_{0}n$$

$$^{1}_{1}H + ^{3}_{1}H \longrightarrow ^{4}_{2}He$$

$$^{3}_{1}H + ^{1}_{0}n \longrightarrow ^{4}_{2}He + \beta^{-}$$

$$^{7}_{3}Li + ^{1}_{1}H \longrightarrow 2\,^{4}_{2}He$$

If the H-bomb is covered in a special metallic sheet and exploded, the effects are worse, because lethal radiations are scattered all around which continue to pollute the environment for months and years to come. A cobalt bomb is an example of this type which is nothing but a cobalt covering of a H-bomb. The neutrons released during explosion interact with metallic cobalt rendering it radioactive and (^{60}Co) is formed.

Fusion reactions do not create fission products, and thus contribute far less to the creation of nuclear fallout than fission reactions but because all thermonuclear weapons contain at least one fission stage, and many high-yield thermonuclear devices have a final fission stage, thermonuclear weapons can generate at least as much nuclear fallout as fission-only weapons.

Only six countries – United States, Russia United Kingdom, People's Republic of China, France and India – have conducted thermonuclear weapon tests. (Whether India has detonated a "true", multi-staged *thermonuclear weapon* is controversial). Thermonuclear weapons are considered much more difficult to successfully design and execute than primitive fission weapons. Almost all of the nuclear weapons deployed today use the thermonuclear design because it is more efficient.

7.27 NUCLEAR REACTOR

Nuclear reactor is device to obtain the nuclear energy in a controlled way to be used for peaceful purposes. We can also say that a nuclear reactor is designed and operated for the purpose of sustaining a nuclear fission chain reaction at a controllable pre-determined rate.

Nuclear reactors are used for the production of heat, mechanical and electrical energy, radioactive isotopes, weapons material and nuclear research.

Working Mechanism

In any nuclear reactor, the heat generated by the controlled fission chain reaction of the nuclear fuel confined in the core of the reactor is transferred to a coolant and this heat energy is used to generate high pressure steam that turns a turbine connected to a generator, thus producing electric power. If the heat energy generated in the fission is utilized for generation electricity, the reactor is known as a power reactor.

Components of a Reactor

A fission reactor consists of five main components.

(a) **Fuel Elements.** The material containing the fissile isotope is called the reactor fuel or nuclear fuel. Its composition can vary from natural uranium to material highly enriched in ^{235}U, ^{239}Pu or ^{233}U. The basic source materials for nuclear fuels are uranium and thorium. ^{235}U present to the extent of about 0.71 percent by weight in the natural uranium is fissile and this is the only natural material from which nuclear energy can be directly produced.

(b) **Moderators.** The function of a moderator in a nuclear reactor is to rapidly reduce (within a fraction of second) the high energy of the fission neutrons. The fast neutrons ejected during fission must be slowed by collisions with atoms of comparable mass which do not absorb them, for efficient fission reaction. The most commonly used moderator is ordinary water, although graphite is sometimes used. The most efficient moderator is helium, which slows neutrons but does not absorb them all. The next most efficient one is "heavy water" (deuterium oxide D_2O), but this is so expensive that it has been used chiefly in research reactor. However, on considerations of price and other properties, H_2O finds favor in many commercial reactors.

(c) **Coolants.** The heat generated in the core of the reactor is removed by a coolant. Both ordinary and heavy water are considered to be good coolants for thermal reactors because of their excellent heat exchange properties. They have also the advantage of serving as both coolants as well as moderators. However due to their low boiling points, high pressures are required to prevent their boiling to high temperatures. Liquid metals such as Na and K are recommended as coolants for use at high temperatures. Various other coolants such as benzene, polyphenyles, air, CO_2, CH_4, H_2 and He are also used.

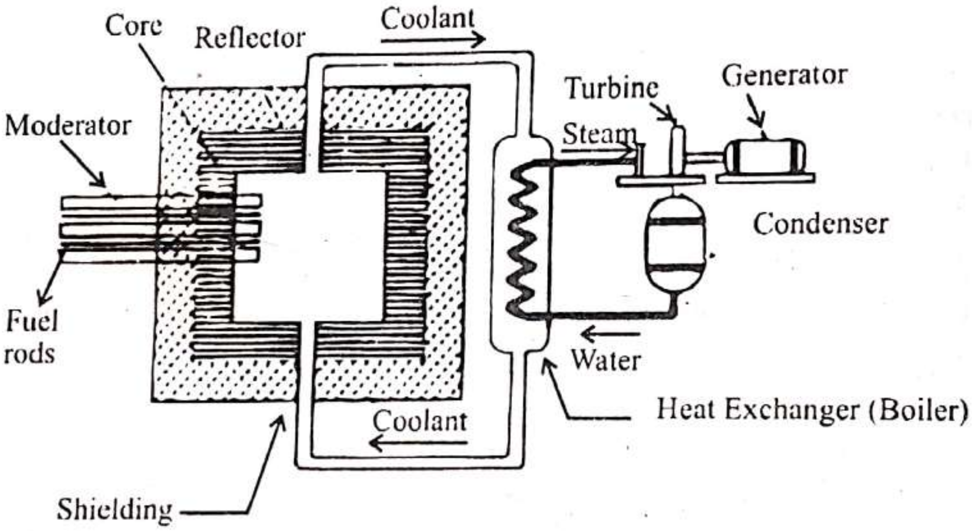


Fig. 7.12. Schematic diagram of nuclear reactor system for generating electric power.

(d) **Control Rods.** The control of power level in a reactor can be achieved by controlling the neutron flux which in turn is achieved by altering the neutron leakage rate or the quantity of fuel in the reactor or by incorporating a suitable neutron absorbing material. Boron is the most common material used for reactor control due to its very high melting point and very large neutron absorption cross section. It is commonly employed in the form of boron steel. Besides boron, cadmium is also used.

(e) **Shielding.** It is an important component of a reactor installation, although it has nothing to do with the operation of reactor. Shielding is provided for attenuation of the gamma rays and neutrons emerging from the reactor which helps to protect the operating personnel from radiation hazards. The shield comprises of a layer of concrete (several feet thick) which surrounds the reactor core. It absorbs both gamma rays and neutrons. It is a good structural material and contains enough hydrogen to moderate the fast neutrons.

7.28 CHARGED PARTICLES ACCELERATORS

From the discovery of nuclear transmutations in 1919 until 1932, the only known sources of particles which could induce nuclear reactions were the natural α - emitters. In fact the only known type of nuclear reactions known during that period of 13 years was the α,p reactions. For example α - emitter $^{210}P_0$ (5.30 MeV, $t_{1/2}$ = 138 days). To carry out the transmutations by using the charged particles as projectiles, some problems are faced. Due to the existence of the Coulomb potential barrier, the charged particles should have sufficient energy to cross the barrier. Using α - particles from naturally occurring sources, a lot of information regarding the construction and structure of nucleus were explored. But for bombardment on heavy target nuclides, charged particles of much higher energy are required. Besides these, the α - particles obtained from natural sources have got no directional properties. Using such particles for the target nuclides placed in a particular direction, very poor results were obtained. To overcome these drawbacks the scientists were experiencing the necessity of having the directed beams of high energy particles. The particles accelerators developed can meat this necessity.

The first device was developed in 1931 by Cockroft Walton by using a voltage multiplier to accelerate the protons. The voltage multiplier ultimately produced a potential difference of about 2 million volts leading to the generation of a 1 – 2 MeV proton beam. In 1931, Van de Graaff developed an electrostatic generator which could produce several million volts of potential difference to accelerate the particles. Presently, the accelerators which do not require any high potential difference are of much importance. Two commonly used charged particles accelerated are discussed below:

1. The Linear Accelerator

The linear accelerator was first developed by Lawrence and Sloan in the united states during 1931. It is a device or machine whereby the kinetic energy of charged particles or ions is progressively increased by multiple acceleration.

A linear accelerator is used to accelerate the protons, electrons, nuclei accelerating them in the electric field. The basic principle involved in this machine is known as resonance acceleration. The charged particles are accelerated in steps. In each step the particles fall through a relatively low voltage in such a way that their velocities are added together in successive steps so that finally they acquire a very high energy of the order of several million electron volt (eV). In linear accelerators charged particles are accelerated by an oscillating electric field applied to a series of electrode with an applied frequency which is in resonance with the motion of the particles.

The linear accelerator consists of a set of cylindrical electrodes of increasing length. Alternate cylinders enclosed in a glass chamber are connected together in such a way that the odd number cylinders are being joined to one terminal and the even number joined to the second terminal of a high frequency power supply. The cylinders are placed is a highly evacuated glass tube.

The ions from the discharge tube at one end move along the axis of the tube and are accelerated by crossing the gap. Suppose the ions are positively charged and moving from left to right. if the first cylinder is positive and second is negative the ions are accelerated and travel through the second cylinder. In the second cylinder the speed will be constant but greater than the first one.

Inside the cylinder the ions are in the field free space and therefore move with constant velocity. The second cylinder is larger enough so that when the ions reach the gap between the second cylinder and third cylinder, the potentials are reversed. The second and third cylinders are positively and negatively charged respectively, hence the ions are again accelerated, in the gap between second and third cylinders.

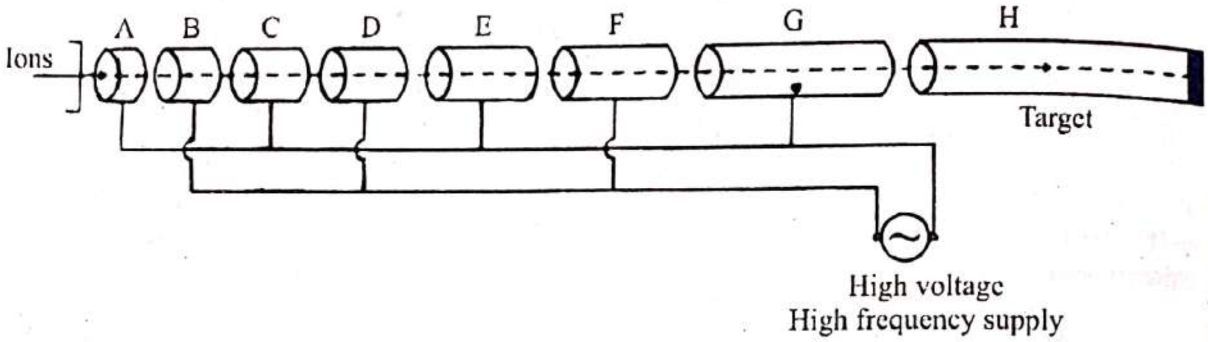


Fig. 7.13. Schematic design of a linear accelerator.

The ions can be kept is phase with the reversal of potentials by making successive cylinders longer than the previous one to allow the increase in the speed of the ions. As a result the ions gain additional energy each time they travel from one cylinder to the next cylinder. The energy in the range of 1 BeV can be obtained by linear accelerators. Due to small size of the magnet the linear accelerator is more suitable for this range of energies.

If V_0 is the initial fixed potential used to accelerate ions into system, and V is the potential difference between the accelerating stages, then ions will have a velocity after the first stage corresponding to an acceleration through $V_0 + V$ volts. After the second stage they will have a velocity corresponding to an acceleration through $V_0 + 2V$ volts and after n stages they will have a velocity corresponding to an acceleration through $V_0 + nV$ volts. Energy after n stages = $\frac{1}{2}$ mv² and the final velocity after n stages.

$$V^2 = \frac{2e}{m}(V_0 + nV) \quad \text{or} \quad \frac{2e}{m}(V_0 + nV)^{1/2}$$

Where m and e are the mass and charge of the ion accelerated. A linear accelerator has the following advantages:

(i) A small magnets can be used

(ii) It is economical for achieving very high energies.

(iii) The particles emitted are in a well-collimated beam.

(iv) A beam of electrons from a linear accelerator can be used to probe the structure of the nucleus.

(v) It can be used to obtain energy in the range of 1 BeV.

However, it suffers from following disadvantages:

(i) The individual particles must pass through a number of alternating fields and a number of power sources. Therefore, many pieces of high frequency apparatus are needed which make the machine more expansive and complicated.

(ii) The ionic current produced is very low-in the order of fraction of micro ampere.

2. The cyclotron

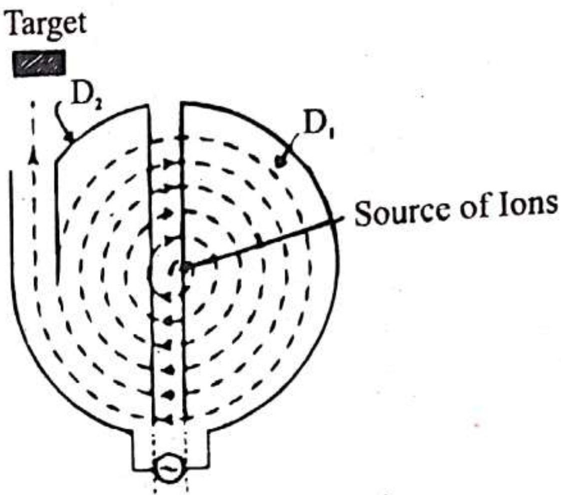


Fig 7.14 Schematic design of a cyclotron

This instrument was also developed by E.O. Lawrence, in the University of California, in 1933 and he was awarded Nobel Prize in this work. This became the most widely used method for the acceleration of charged particles (positive ions). The cyclotron also uses multiple acceleration of ions and in many respects it can be thought of as a linear accelerator which has been wrapped around itself in a spiral. The drift tubes are replaced by two flat hollow semicircular electrodes called *dees* because of their resemblance to the letter "D". These dees which are connected to a radio frequency oscillator, are contained is a large flat vacuum tank between the poles of an electromagnet. (Fig 7.14)

The particles or ions to be accelerated in cyclotron are introduced into the space between dees where they are attracted by the applied electric field into one of the dees. From dees they drift in an electrically field force region. The ions are confined to a semicircular path by the magnetic field, and if they emerge from the dees after a period of time corresponding to half of the period of oscillation, they will be accelerated across the gap between the dees and into the second dee where they will follow another semi circular path. This process is repeated many times, the ions following orbits of increasing radius after each successive acceleration until they reach the perimeter. Here they are deflected from their circular path by a negatively charged electrode and energy though a thin aluminium window.

The operation of the cyclotron depends upon the ions taking exactly the same interval of time, i.e., half of the period of the applied oscillation. on each semi-circular path.

The equation of motion of an ion of mass m charge 'e' and velocity 'V' in a magnetic field 'H' is given by the necessary equality of the centripetal magnetic force HeV and the centrifugal force $\frac{mV^2}{r}$, where 'r' is the radius of the ion's orbit.

Centripetal magnetic force = centrifugal force.

$$HeV = \frac{mV^2}{r}$$

$$r = \frac{mV^2}{HeV}$$

$$r = \frac{mV}{He} \qquad (7.33)$$

We also know that angular velocity ω is equal to $\frac{V}{r}$

$$\omega = \frac{V}{r}$$

$$\omega = \frac{He}{m} \quad \left(\because \frac{V}{r} = \frac{He}{m}\right) \qquad (7.34)$$

From Eq. (7.34) it is evident that the angular velocity is independent of radius of ion and velocity V, and that the time required for half a revolution is constant for ions of same e/m, provided that the magnetic-field strength is constant. In practice, the magnetic field is kept constant, e/m is a characteristic of the type of ion used, and therefore ω is constant.

In the cyclotron, as in the linear accelerator, multiple acceleration by a radio frequency (r.f.) potential is used. The radio frequency has to be chosen such that its period equals the time it takes for the ions to make one revolution.

$$\upsilon = \omega/2\pi$$

It is also clear from Eq. (7.34) that in a given cyclotron, both the magnetic field and oscillating frequency can be left unchanged when different ions of same e/m e.g. (deuterons and α – particles) are accelerated.

Most cyclotrons are operated as electrons sources and they often use r.f. oscillators tuned to about 11 or 12 mega cycles/sec for deuterons.

By squaring Eq. (7.33) and multiplying by $\frac{1}{2m}$ on both sides

$$r^2 = \frac{m^2V^2}{H^2e^2} \quad \text{or} \quad m^2V^2 = H^2e^2r^2$$

$$K.E = \frac{1}{2}mV^2 = \frac{H^2e^2}{2m}r^2$$

Thus the final energy attainable for a given ion varies with the square of the radius of the cyclotron. With H = 15,000 gauss the deuterons energy = $0.035\ r^2$.

A very important feature of the Cyclotron is the focusing action it provides for the ion beam. The electrostatic focusing at the dee gap is entirely analogous to that in the high voltage accelerating tubes. However, as the energy of the ion increases this effect becomes almost negligible.

Limitations:

The energy gained by the ions in the Cyclotron depends upon the radius of the dees. The greater the radius, the greater the energy gained by the particle. At higher energies, the velocity of the particle becomes so large that $V/_c$ becomes appreciable, where c is the velocity of light. Thus the mass of the particle starts increasing in accordance with the relation.

$$m = \frac{m_0}{\sqrt{1-\frac{V^2}{c^2}}} \quad \text{where } m_0 = \text{rest mass of the ion.}$$

This increase is about $\frac{1}{2}$ percent for a 10 MeV deuteron and about 5 percent for a 100 MeV. Thus the particle goes out of step in the cyclotron.

Why cyclotron is not suitable for accelerating electrons?

Electrons, having very small masses, move with nearly the speed of light at a relatively low energy. Therefore the electrons cannot be accelerated in a cyclotron, because of the high frequencies that would be required and because of the enormous relativistic mass increase of electrons even at moderate energies e.g. At 1MeV the total mass is three times the rest mass. The first device for producing electron energies above 2 or 3 MeV was the betatron, first developed by D.W. Kerst in 1940.

7.29 RADIATION HAZARDS AND SAFETY MEASURES

The ionization of atoms or molecules results from the passage of nuclear radiation through matter, a single α, β, or γ – ray producing about 100,000 ion pairs. A secondary effect of ionization in molecules is the rupture of chemical bonds causing the destruction of the chemical compounds from which living tissue is composed.

In handling radioactive materials, two distinct types of hazard should be distinguished and appreciated. These are:

(a) Contamination hazards involving ingestion of very small quantities of radioactive material, and

(b) Radiation hazards involving exposure to some external source of radiation.

(a) Contamination Hazards

The factors which influence the radio-toxicity of a nuclide as a contamination hazard if ingested orally, by inhalation, by absorption through the skin, or directly into the blood stream – as a result of an accident – are:

(a) The type of radiation emitted, α and β being the worst.

(b) The physical properties of the materials, for example the chances that a compound ingested orally will enter the blood stream, and so be deposited in a vital organ, will be reduced if it is an insoluble compound.

(c) The chemical properties of the nuclide.

(d) Half-life of the nuclide. A composite "effective" half-life which takes into account both radioactive and biological half-lives can be determined from:

$$\frac{1}{\text{effective half-life}} = \frac{1}{\text{radioactive half-life}} + \frac{1}{\text{biological half-life}}$$

A few examples of effective half-lives are given in Table 7.8. Because of biological retention properties associated with many nuclei there is a long term accumulative effect and therefore, the quantities of these materials which constitute a hazard are often extremely low.

Table 7.8

Nuclide	Concentrates	Half-life (in days)		
		Radioactive	Biological	Effective
Sodium-24	Whole body	0.62	19	0.61
Iodine-131	Thyroid	8.1	180	8.1
Strontium-90	Bone	9.1×10^3	3.9×10^3	2.7×10^3
Radium-226	Bone	5.9×10^5	1.6×10^4	1.6×10^4

(b) Radiation Hazards

The radiation hazards associated with most chemical and tracer work will be small or negligible. They mainly arise from isotope stock storage and from sealed sources such as those used as radiation sources for radiation chemistry studies. Under no circumstances should the combined effect of all the sources of activity be permitted to involve a weekly, gross exposure to any person in excess of 100 milli roentgens and, indeed, the aim should be to maintain conditions such that the total radiation does cannot exceed a tenth of this value. Film badges can-and frequently are-worn in order to measure the accumulated weekly dose. They do, however, only measure what has already occurred, and in this respect, they are a poor substitute for careful radiation monitoring to anticipate radiation exposure.

Exposure to radiation hazards is minimized by one or more of the following methods:

(a) Using minimum necessary quantities of active material and limiting exposure time.

(b) Making full use of the inverse square by remaining at a distance and by using forceps or tongs where necessary to achieve this end.

(c) Employing adequate shielding – particularly in the case of fixed irradiation installations.

Rules and regulations concerning the use of radioactive material can at no time substitute for anticipation of hazards, care in manipulations and "good housekeeping". With proper thought and care a radiochemical laboratory can be as safe as more conventional organic and inorganic laboratories.

Safety Measure of Nuclear Hazards

Exposure to high levels of nuclear radiation can cause sickness or death. Because people cannot see, hear, smell taste, or feel nuclear radiation. They are unable to tell without the proper radiological instruments whether the levels of radiation around them might be harmful.

High energy radiations, coming out of radioactive substances, can cause chemical changes is biological systems. Living systems are composed of a sufficient quantity of water which gets radiolysed on interaction with alpha, beta and gamma rays of high energy and ions such as H_2O^+ are produced. When these ions interact with any negatively charged species such as an election, they generate a highly excited neutralized molecule which stabilizes itself by immediate fragmentation into a hydrogen atom and a hydroxyl radical.

$$H_2O^+ + e^- \longrightarrow H^*{}_2O \longrightarrow H + OH^*$$

This is one of many possible reactions that my occur as a consequences of radiation interaction with water and other molecules which constitute the living organisms. The overall effect is the formation of ions, atoms and free radicals. Their resulting species are highly reactive and can destroy protein and other molecules present in the living matter. Fore example, free radicals can damage the hydrogen bonds and sulphur-sulphur pivotal in maintaining the critical conformation of protein. Such a reaction will bring about protein destruction which will curtail its role as an enzyme and thus metabolic processes and cell division will be abnormal, penetration of substances into and out of the cells can take place to such an extent that organisms are injured.

Units for radiation Exposure

There are several units which are employed to estimate the radiation damage on biological systems as described below;

The unit of radiation dosage that was originally used in measuring biological damage is the roentgen (symbol r). One roentgen is the radiation that produces one electro static unit (esu) of pairs of positives and negative ions in 1 cm^3 of air as S.T.P (standard temperature and pressure).

The ionization efficiency and the mode of absorption vary with the nature of radiation and the corresponding exposure effects also differ. This is because an alpha particle emitted within a cell will deposit its energy entirely within that cell, whereas gamma rays will be only fractionally consumed by any biological tissue. The greater the amount of energy deposited per cell, the greater is the biological damage.

International commission on radiological protection for various types of radiations have adopted maximum permissible doses for human beings occupationally exposed to external radiations. They have adopted two different standards for whole body exposure and limited body period of 13 consecutive weeks for the people over the age of 18, with the additional restriction that the total accumulated dose should not exceed 5 (N – 18) rem, where N is the age of the recipient in years. For the case of limited exposure the hands and forearms or feet and ankles, the corresponding figures are 25 rem and 75 (N – 18) rem. However, the radiation exposure may also occur by ingestion. The most likely means of ingesting radioisotopes may also occur by ingestion. The most likely means of ingesting radioisotopes can be (1) inhalation of contaminated air (2) drinking of contaminated water (3) entry through open wounds. Radioactive substances when ingested or inhaled become fixed in the body for varying lengths of time. All care must therefore be taken to avoid intake of radioactive materials.

7.30 APPLICATIONS OF TRACERS IN CHEMISTRY

Many radioactive isotopes are very much useful in different disciplines such as research, medicine, analytical problems of Chemistry etc. It is a well-known fact that the physico-chemical properties of a radioactive atom are almost identical with those of its inactive atoms. This characteristic property of a radioisotope helps to locate isotopes when the former is added to the ordinary chemical elements consisting of a mixture of inactive isotopes. The added radioisotope is called *isotopic tracer* or the *radioactive indicator*. The tracer added to a system is often referred to as a label or a tag, and the traced material is said to be *labeled or tagged*.

The use of tracer in chemical research and analytical chemistry forms a special type of method called the *tracer technique*. Tracer technique is the method of using an isotope of an element to study a physical or a chemical change. The change is monitored by following a characteristic property-mass or radioactivity of the isotope used. This technique is based on the following important factors.

(i) The chemical properties of radioactive isotopes are similar to that of the corresponding non-radioactive elements.

(ii) The nature of the radioactivity of a radioisotope is capable of tracing, identifying, and determining the position of the corresponding atom among excess of non-radioactive elements.

(iii) This technique helps to detect very small quantities that are many times smaller than these elected by any other known physical or chemical method.

The tracers many be either radioactive or separated stable isotopes and their use as tracer is based on the two requirements; (a) it must represent the element being traced at the time of measurement, and (b) it must be distinguishable from the element being traced. While using radioisotopes as tracers, it is necessary to choose isotopes with half-lives which are neither too short nor too high. This is because of the fact that the time of observation is limited in case of short-lived isotopes, while the intensity of radiation emitted is very less, which cannot be detected early in case of long-lived isotopes. Usually isotopes having half-lives roughly between a four hours to few thousand years are used as tracers.

When a non-radioactive, heavy isotope is used as the tracer, then the mass is monitored in the tracer technique. The use of radioactive tracer is preferred in tracer technique because its radioactivity can be accurately measured during the physical or chemical process. The commonly used isotopic tracers are listed in Table 7.9.

Table 7.9. Common isotopic tracers.

Tracer Element	Tag	Detection
Hydrogen	$^{2}_{1}H$ $^{3}_{1}H$	Mass β – particle
Oxygen	$^{18}_{8}O$	Mass
Carbon	$^{13}_{6}C$ $^{14}_{6}C$	Mass β – particle
Nitrogen	$^{15}_{7}N$	Mass
Sodium	$^{24}_{11}Na$	β – particle
Phosphorus	$^{32}_{15}P$	β – particle
Iodine	$^{131}_{53}I$	β – particle

Isotopic labeling technique is discussed below for some representative cares.

(i) $^{14}_{6}C$ – labelling

$$^{14}_{7}N + ^{1}_{0}n \longrightarrow ^{14}_{6}C + ^{1}_{1}H$$

(ii) $^{36}_{17}Cl$ – labelling

$$^{35}_{17}Cl + ^{1}_{0}n \longrightarrow ^{36}_{17}Cl + \gamma$$

(iii) $^{32}_{15}P$ – lebelling

$$^{31}_{15}P + ^{1}_{0}n \longrightarrow ^{32}_{15}P + \gamma \text{ and } ^{32}_{16}S + ^{1}_{0}n \longrightarrow ^{32}_{15}p + ^{1}_{1}H$$

Some important applications of radioactive isotopes as tracers are discussed below:

1. Medical Uses

Several radioactive isotopes are used successfully in checking growth of or removing the cancerous cell. Since radioisotopes of an element have the same chemical properties as stable isotopes of the same element, they can be used to 'label' an element in a compound. A radiation detector can be used to follow the path of the element throughout the body. Salt solution containing sodium-24 can be injected into the blood-stream in order to follow the flow of blood and locate obstructions in the circulatory system. Thallium-201 tends to concentrate in the healthy heart muscle tissue, while technetium-99 concentrates in the abnormal heart tissue. Iodine-131 concentrates in the thyroid gland, the liver and certain parts of the brain, and is used to monitor goiter and other thyroid problems, as well as liver and brain tumors. Cobalt-58 is used to determine uptake of vitamin B12, while cobalt-60 is used for the radiation treatment of cancer.

2. Research Applications

Stable as well as radioactive isotopes are frequently used in tracing out the correct path of chemical and physiological reactions, some of which are described below:

(a) If radioactive sulphur-35 ion is added to a saturated solution of cobalt sulphide in equilibrium with solid cobalt sulphide, the solid becomes radioactive. This indicates that sulphide ion exchange occurs between solid and solution in solubility equilibrium.

$$CoS_{(s)} \rightleftharpoons Co^{2+}{}_{(aq)} + S^{2-}{}_{(aq)}$$

(b) Photosynthesis is the process by which green plants synthesize carbohydrates from carbon dioxide and water in the presence of light.

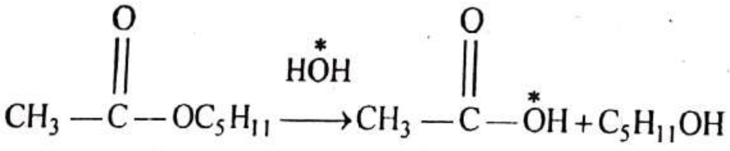
$$6CO_2 + 6H_2O \xrightarrow[\text{chlorophyll}]{\text{sunlight}} C_6H_{12}\,O_6 + 6O_2$$

In the mechanism of photosynthesis the important point is that the molecular oxygen in the product is coming from water and not from carbon dioxide molecule. By studying the reaction with labeled oxygen, the product oxygen can be identified.

$$6CO_2 + 6H_2O^* \longrightarrow C_6H_{12}O_6 + 6O_2^*$$

(c) The mechanism of ester hydrolysis can be studied by making use of labeled water ($H_2^{*}O$). Theoretically an ester may be hydrolyzed in two different manners to form an acid and alcohol.

(i)



$$CH_3-\overset{O}{\overset{\|}{C}}-OC_5H_{11} \xrightarrow{H\overset{*}{O}H} CH_3-\overset{O}{\overset{\|}{C}}-\overset{*}{O}H + C_5H_{11}OH$$

The labeled oxygen appeared only in the acid, showing that — OC_5H_{11} group is substituted by — *OH in the hydrolysis.

(d) Phosphorus – 32 when present in the phosphate fertilizer has been used to investigate the rate and manner of the absorption of fertilizer. Moreover, by such studies we may know separately about the proportion of plant's phosphorus coming from soil and from the fertilizer, and thus about the kind of fertilizer which is best for a given soil and crop.

3. Industrial Applications

There are many applications of radiochemistry in industry and engineering, some of them will be mentioned here.

(a) Addition of a small amount of phosphorus-32 to the iron ore is used in steel industry for detecting all the phosphorus impurity present in the original ore.

The disappearance of radioactivity from the molten steel indicates the removal of the phosphorus.

(b) Radioisotopes have been used in studying the wear and lubrication of motor car engines. In practice, piston rings are made radioactive by irradiating them in a nuclear reactor; they are then assembled into an engine. Engine is allowed to run and the oil is tested regularly for the appearance of radioactivity caused by the presence of tiny bits of metal from wearing off of the piston rings.

(c) The radiation passing through a material decreases as the material gets thicker. Thus the amount of penetrating radiation can be used to estimate the thickness of various materials such as paper or plastic etc.

(d) A similar use of radioactive isotopes is made in level gauges and empty packet detectors. The level of a liquid in a closed vessel can be found by placing a source on one side of the container and detector on the other. These are then moved down, a sudden decrease in the detected radiation shows the level of the liquid. Level gauges of this type are used to measure the level of liquids in fire extinguishers and gas cylinder. Similarly empty packet detectors can be used to reject empty or insufficiently filled packets of cigarettes or biscuits.

(e) Radioactive isotopes can be used to detect leaks in pipelines of water. For this purpose sodium-24 is used. Solution containing radioisotopes is injected into the pipeline and the points where the leakage into the surrounding soil has occurred can be scanned from the surface using a detector.

4. Radioactive Dating

The ages of articles of organic origin can be estimated by radiocarbons dating. The radioisotope carbon-14 is produced continuously in the upper atmosphere, as nitrogen atom captures cosmic-ray neutron.

$$^{14}_{7}\mathrm{N} + ^{1}_{0}\mathrm{n} \longrightarrow ^{14}_{6}\mathrm{C} + ^{1}_{1}\mathrm{H}$$

The $^{14}_{6}\mathrm{C}$ atoms thus produced are rapidly oxidized to $^{14}_{6}\mathrm{CO}_2$ which in turn is incorporated in plants as a result of photosynthesis. Thus all plants contain some $^{14}_{6}\mathrm{C}$ and since the carbon of animals is ultimately derived from plants, the carbon of animal will contain the same ratio of $^{14}_{6}\mathrm{C}/^{12}_{6}\mathrm{C}$ as the carbon of plants. When the plant or animal dies, the $^{14}_{6}\mathrm{C}$ isotope is no longer absorbed from the atmosphere (in case of plant) and plants (in case of animal). After this the amount of $^{14}_{6}\mathrm{C}$ in the dead tissues starts decreasing due to its radioactivity.

$$^{14}_{6}\mathrm{C} \longrightarrow ^{14}_{7}\mathrm{B} + \beta^-$$

To determine the age of a sample, the activity per minute per gram of carbon is measured. Now thus knowing the half life, the approximate time of the death of the plant or animal can be calculated according to the following disintegration equation:

$$T = \frac{1}{\lambda} \ln \frac{N_0}{N}$$

This technique was first used by Willard Libby (Nobel Laureate) to determine the age of wood or animal fossils. The carbon-14 technique is useful only for dating objects less than 50,000 years. Older objects possess too little activity to be dated accurately.

Example 7.8. The amount of ${}^{14}_{6}C$ isotope in a piece of wood is found to be one sixth of its amount present in a fresh piece of wood. Calculate the age of wood (half-life of ${}^{14}_{6}C = 5577$ years).

Solution

Let $N_0 = 1$ then $N = \frac{1}{6}$

$$t_{1/2} = 5577 \text{ years}$$

$$\lambda = \frac{0.693}{t_{1/2}}$$

or $$\lambda = \frac{0.693}{5577} \text{ year}^{-1}$$

$$t = \ln \frac{1}{\lambda} \text{ in } \frac{N_0}{N}$$

or $$t = \frac{5577}{0.693} \ln \frac{1}{1/6} = \frac{2.303 \times 5577}{0.693} \log 6$$

or $$t = 20{,}170 \text{ years}$$

5. Age of the Earth

The natural radioactive decay series indicate that all the ${}^{238}U$ present in nature would ultimately be converted to lead. Thus a naturally occurring uranium mineral is associated with some non-radioactive lead, formed from uranium. The rocks on Earth are assumed to be formed from magma (molten rock). It was then the radioactive uranium in the rock must have started decaying. Therefore, by estimating the ratio of ${}^{206}Pb/{}^{238}U$ by weight, the age of rock and hence that of Earth can be found out. The half-life of ${}^{238}U$ is 4.49×10^9 years. This isotope forms ${}^{206}_{82}Pb$ though a series of steps and the overall reaction on is

$${}^{238}_{92}U \longrightarrow {}^{206}_{82}Pb + 8\,{}^{4}_{2}He + 6\bar{e}$$

Based on this equation for every 238 grams of uranium decayed, 206 grams of lead must be present in the sample rock. This age estimation is based on the assumption that initial radioactive material, the final stable nucleus, and all the members of decay series remain in the rock and the Pb-206 present is the rock is the product of U-238 decay.

6. Agricultural Applications

Radioactive isotopes have been widely used in Agriculture to improve the plant growth. Radioactive P-32 is added with phosphate fertilizers to the soil to improve plant growth. The uptake of ^{32}P from soil by plants is determined by measuring the radioactivity in different parts of the plants. The total amount of the phosphorus taken up by whole plant is determined by chemical analysis and that of the added fertilizer by the activity measurement. The difference is the natural phosphorus present in the soil. By using various P-32 label phosphates, it has been shown that ammonium phosphate is much more efficient fertilizer than super phosphate and calcium phosphate.

It is also possible to investigate the relationship between root growth and the phosphorus up take by placing fertilizer labeled with ^{32}P at different depths and distances from growing plants. The radioactive carbon (^{14}C) has been helpful in understanding the mechanism of photosynthesis in plants. By using $^{14}CO_2$ with $^{12}CO_2$ it has been shown that the oxygen which is formed along with sugars, comes from water and not from carbon dioxide.

Radioactive tracers iron has been used to investigate the disease chlorosis developed in plants because of the shortage of chlorophyll. Isotopic tracers have also been used in studying animal nutrition and metabolism. Many fungicides contain sulphur. The use of ^{35}S tracer indicates the advantages and disadvantages caused by these fungicides.

QUESTIONS

Q.1. (a) What is nuclear chemistry? Discuss its significance.

(b) Write a short note on the atomic nucleus.

(c) Discuss various models of nucleus composition.

Q.2. (a) Explain some properties of nucleus.

(b) Write a short note on fundamental particles present with in the nucleus.

Q.3. (a) Why certain isotopes are stable while other are radioactive? Discuss various factors affecting nuclear stability.

(b) Explain the difference between mass defect and binding energy.

(c) Calculate the binding energy of $^{6}_{3}Li$ in MeV per atom if the exact mass of the nuclide is 6.01512 amu. (An 32.02 MeV/atom 5.34 meV/nucleon)

Q.4. (a) What are nuclear models? Explain the liquid drop model in detail.

(b) Elaborate nuclear shell model. Discuss its advantages and limitations.

Q.5. (a) What are various types of radiation given off by a radioactive element. Discuss their main characteristics.

(b) Give an account of the methods available for the detection and measurement of radiation.

Q.6. (a) What are ionizing radiations? How do these interact with matter?

(b) Write a short note on radiation dosimetry.

Q.7. (a) What are dosimeters? Explain Fricke dosimeter.

(b) Discuss the kinetics of radioactive decay.

(c) Radioactive kinetics follows first order reaction, comment.

Q.8. (a) What is decay constant and half-life? How are these interrelated?

(b) How do half life and decay constant determine experimentally.

(c) The half life of $^{32}_{15}P$ is 14.3 days. How long it would take for 1g of sample of $^{32}_{15}P$ to decay to 0.5g of ? (Ans. 14.3 days)

(d) Calculate the half life for decay of $^{39}_{17}Cl$ if 1g of sample decays to 0.125 g in 165 min. (Ans. 55 min)

Q.9. (a) What is nuclear decay? Explain various types of nuclear decay.

(b) What is mean life? Derive the relationship between mean life and decay constant.

Q.10. (a) Discuss theory of radioactive disintegration.

(b) Write a short note on artificial radioactivity.

Q.11. (a) What is radioactive equilibrium? Discuss the kinetics of a radioactive equilibrium.

(b) Explain the difference between transient and secular equilibrium.

Q.12. (a) What is a nuclear reaction? How does it differ from a chemical reaction?

(b) What is nuclear fission? Explain nuclear fission with full detail.

(c) Why neutrons are the ideal bullet for fission process?

(d) What is atom bomb? Explain its working principle.

Q.13. (a) What is nuclear fusion? Give a detail of fusion reactions occurring in stars and sun.

(b) What is hydrogen bomb? Explain its working principle.

(c) Compare nuclear fission with nuclear fusion.

Q.14. (a) What is nuclear reactor or atomic pile?

(b) Explain its various components.

Q.15. (a) What are charged particles accelerators? Why do these needed?

(b) What is the linear accelerator? Discuss its working principle and limitations.

(c) Explain the working of cyclotron with suitable diagram.

(d) Why cyclotron is not suitable for accelerating electrons?

Q.16. (a) What are diffent hazards associated with nuclear radiations?

(b) Discuss various safety measures for nuclear hazards.

Q.17. (a) What are tracers? What are the requirements for an isotope to be used as tracer?

(b) Write a detailed accent of various applications of tracers in chemical and other sciences.

Q.18. Justify/comment on the following statements:

(i) The future of mankind is in the hands of nuclear scientists.

(ii) Curie is the SI units of radioactivity.

(iii) Lighter nuclides have more binding energy.

(iv) Radionuclides are intrinsically unstable.

(v) All radioactive decays follow first-under kinetics.

(vi) Nuclear fission is a sustainable reaction.

(vii) Water is used as moderator in atomic pile.

(viii) $\alpha-$particles have more penetrating power.

(ix) $\beta-$particles have more ionizing power.

(x) Radiations can damage human skin.

(xi) Radiation can be used for diagnostic purposes.

(xii) Atomic bomb uses nuclear fission reaction.

(xiii) H-bomb works on the principle of nuclear fusion.

(xiv) Radiation dosimeters are used to measure the amount of radiation damaged.

(xv) Heavy nuclides usually decay by $\beta-$decay.

REFERENCES

1. Friedlander, G., Kennedy, J.W., Macias, E.C. and Miller, J.M. 2002. Nuclear and Radiation Chemistry. John Wiley & Sons, New York.
2. Gopalan, R. 2003. Elements of Nuclear Chemistry. Vikas Publishing House, Pvt, Limited, New Delhi.
3. Lieser, K.H. 1999. Nuclear and Radiochemistry. John Wiley & Sons, New York.
4. Choppin, G.R., Liljenzin, J.O., and Rydberg, J. 2001. Radiochemistry and Nuclear Chemistry. Butter-Worth-Heinemann, USA.
5. Loveland, W., Morrissey, D.J. and Seaborg, G.T. 1998. Modern Nuclear Chemistry. Wiley-Intersciences, Inc, New York
6. Arnikar, K.H. 1999. Essentials of Nuclear Chemistry. New Age International Publisher, New Delhi.

Chapter 8

MOLECULAR SYMMETRY

بت تراش / مجسمہ ساز   ترتیب   معیار

8.1 INTRODUCTION

The word symmetry comes from the Greek word *syn-metron,* to measure together. This means that we consider two or more things to observe symmetry. From ancient times the concept of symmetry is prevalent in philosophy, natural sciences and mathematics. Long ago the Greek sculptors and architects were associating the term symmetry with the idea of beauty and harmony. This concept had become popular during the time of Pythagorus. He distinguished between evenness and oddness, between true statement and false statement and so on. Plato, the Greek philosopher, felt that the world consists of earth, water, fire and air. According to him the earth is a cube, the fire a tetrahedron, the water an icosahedron and the air an octahedron.

غالب

برابری

جفت

ناقابلِ غور

Symmetry is a widely distributed property in nature. Nature provides countless examples of symmetry. For example sun flower possesses a kind of symmetry. A plant leaf also possesses a definite symmetry. Similarly the external shape of a crystal indicates a regular interval arrangements of atoms ions or molecules. The human body is also symmetric in nature. We the human beings, also like regular and symmetric objects. It seems that a certain love for regularity is built in human nature. That is why we love those objects which possess regularity in their shape as compared to randomly shaped objects.

Symmetry is associated with regularity in form, pleasing proportions, regular repetition of certain characteristics or a harmonious arrangements: thus it is associated with the sense of beauty.

مستطیل   مربع

Symmetry is present in geometrical figures, crystalline solids and molecules. Consider two geometrical figures, the rectangle and the square. The square is said to be more symmetrical than the rectangle due to the fact that all the sides of square are equal, whereas in rectangle opposite sides are equal. One can quantitatively say that the square is more symmetrical due to the presence of large number of symmetry elements and symmetry operations in it.

The study of symmetry is of great significance in connection with both theoretical and experimental studies of molecular structure. The basic principles of symmetry are applied in quantum mechanics, spectroscopy and structure elucidation by X-ray, neutron and electron diffraction. Knowing the symmetry of the molecule one can predict the IR and Raman spectrum of a molecule and knowing the spectrum one can arrive at the symmetry or structure of a molecule. Nature exhibits a great deal of symmetry, and this is specially evident when we examine molecules in their equilibrium configuration. By equilibrium configuration, we refer to that with the atoms fixed in their mean positions. When symmetry is present, certain calculations are simplified if symmetry is taken into consideration. Aspects of symmetry also determine whether a molecule is optically active or have a dipole moment. The mathematical tool which makes use of symmetry is the group theory. Group theory is the systematic discussion of symmetry. Modern treatments of rotational vibrational and electronic spectroscopy of molecules all make extensive use of group theory.

8.2 DEFINING THE COORDINATE SYSTEM

In our discussion, it will be necessary to define a coordinate system for movement of molecules. In all cases will be adopted a standard Cartesian coordinate system with axes x, y and z defined by the so called "*right-hand rule*." By this convention, the positive directions of the three cardinal axes are defined in the same sense as the thumb, index fingers and middle finger of the right hand when extended so that they are mutually perpendicular to each other. Hold your right hand so that your thumb is pointing up, extend your index finger as if pointing a gun and bend your middle finger so that it is perpendicular to the other two. Your thumb, index finger, and middle finger now corresponds, respectively to z, x and y directions of the Cartesian coordinate system (Fig.8.1).

The orientation of a molecule's bonds and bond angles relative to the coordinate system is often defined on the basis of symmetry of molecules. Generally the following conventions are observed:

(i) The origin of the coordinate system is located at the central atom or the centre of the molecule.

(ii) The z-axis is collinear with the highest-order rotational-axis (the principal axis). If there are several highest-order rotational axes, z is usually taken as the axis passing through the greatest number of atoms. However, for a tetrahedral molecule the x, y and z are defined as collinear with the C_2 axes.

(iii) For planar molecules, if the z-axis as defined above is perpendicular to the molecular plane, the x-axis lies in the plane of the molecule and passes through the greatest number of atoms (e.g. square planar, XeF_4). If the z-axis lies in the plane of the molecule, then x-axis stands perpendicular to the plane. (e.g. bent H_2O molecule)

(iv) For nonplanar molecules, once the z-axis has been defined, the x-axis is usually chosen so that the xz plane contains as many atoms as possible. If there are two or more such planes containing identical sets of atoms, any one may be taken as the xz plane.

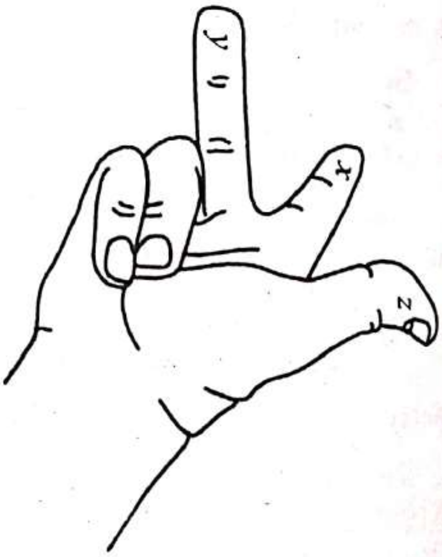


Fig.8.1 Way of assigning, the thumb, index finger and middle finger of right hand for the axis orientations of a Cartesian coordinate system

It is important to realize that these are conventions and not rules. In texts, you may find different choices of axis orientation for same molecule system. In such cases, the qualitative and quantitative results based on the symmetry arguments will be same.

8.3 SYMMETRY ELEMENTS AND SYMMETRY OPERATIONS

The two things, symmetry elements and symmetry operations, are closely related, and therefore are often confused. They are, however, different kinds of things, and it is important to grasp and retain, from the outset, a clear understanding of difference between them. The symmetry of a molecule or ion is defined in terms of symmetry elements and symmetry operations.

A symmetry element is an imaginary geometrical entity such as a line, a plane, or point about which a symmetry operation can be performed. A symmetry operation is a movement of an object about a symmetry element such that the object's orientation and position before and after the operation are indistinguishable. In other words, if we note the position and orientation of an object before and after a movement is carried out, the movement is a symmetry operation if these two positions and orientations are indistinguishable. This means that the operation carries every point of the object into an equivalent point or back into the identical point. One final way in which we can define a symmetry operation is to say that its effect is to take the body into an *equivalent configuration*. By equivalent configuration we mean one which is indistinguishable from though not necessarily identical with the original.

Symmetry elements and symmetry operations are so closely interrelated because the operation can only be defined with respect to the element, and at the same time, the existence of a symmetry element can be demonstrated only by showing that the appropriate symmetry operations exist. The symbols for the symmetry operations are the same as these for the symmetry elements, but in literature operations are given a caret like quantum mechanical operator, because they can be applied to wave functions.

The symmetry of an object can be described by listing all the symmetry operations it possesses. The number of operations can be as few as one (the identity), or as many as infinity. The operations are referred to as identity (E), rotation (sometimes called proper rotation (C_n), reflection (σ), inversion (i) and rotation-reflection (sometimes called improper rotation) (S_n). All the symmetry elements for an object pass through a common point at the centre of the object. Therefore, the symmetry of an isolated molecules or ions is referred as *point group symmetry*. The relationship between symmetry elements and symmetry operations is described in Table 8.1

Table 8.1 The symmetry elements and the corresponding symmetry operations

Symmetry Elements	Symmetry Operations
Proper axis of symmetry (C_n)	Rotation once or several times by an angle $\theta = (2\pi/n)$ about the axis.
Plane of symmetry (σ)	One or more reflection in the plane.
Improper rotation (S_n)	Rotation about the axis followed by reflection in the plane perpendicular to the rotation axis.
Centre of symmetry (i)	Inversion of all atoms through the centre of symmetry
Identity (E)	This operation leaves the molecules unchanged.

8.4 IDENTITY ELEMENT

The simplest of all symmetry operations is identity, given the symbol E. This operation leaves the molecule or object unchanged. If a sequence of symmetry operations brings the molecule or object back to its original configuration, the net operation is called identity operation. Every object possesses identity. If it possesses no other symmetry, the object is said to be *asymmetric*. As an operation, identity does nothing to the molecule. It exists for every object, because the object itself exists. The need for such an operation arises from the mathematical requirements of group theory. Of more immediate concern, identity is often the result of carrying out a particular operation successively a certain number of times. In other words, if you keep doing the same operation repeatedly, eventually you may bring the object back to the identical orientation from which you started. Thus, if a series of repeated operations carries the object back to its starting point, the result would be identified simply as identity. For example, two successive rotations about the C_2-axis in water are equivalent to identity. This fact is expressed as $C_2^2 = E$. Also $C_v^2 = E$, $C_v'^2 = E$. Each of the elements E, σ and i generates only one operation because two successive i or σ operations bring back the molecule or object to its original configuration.

$$\sigma^2 = E, \quad i^2 = E$$

8.5 PROPER AXIS OF SYMMETRY/PROPER ROTATION

The proper axis of symmetry or proper rotation is designated by C_n, where rotation about an axis by $2\pi/n$ radians (360°/n) brings the molecule or object back to an equivalent position. The value of n is referred to as the *order* of rotation. By order is meant the value of n in $(2\pi/n)$ such that the rotation through $2\pi/n$ gives an equivalent configuration. In other words, a molecule or object is said to possess a proper rotational axis if a rotation through $2\pi/n$ radians (360°/n) brings the molecule to a equivalent position. The corresponding element is referred as an n-fold rotation axis. The value of n can vary from 1 to infinity (∞) for various molecules.

The value of n = 1 corresponds to a rotation through an angle 2π, which means doing nothing on the molecule. In other word, C_1 means an identity operation E which leaves the molecule unchanged. Other examples of molecules having C_1 axis are CH_3CHO, HNClF, HCFBrCl etc.

Water (H_2O) and hydrogen sulphide possess C_2 axis of rotation or symmetry. The z-axis in water molecule is a two-fold axis of symmetry. A rotation through $2\pi/2$, i.e., 180° about this axis is called the C_2 operation. Consider water molecule to be placed on the plane of paper and it is rotated 180° about an axis passing through the oxygen atom and bisecting the angle between two H-atoms. The new orientation is superimposable on the original one. It may be observed that the new orientation produced by 180° rotation is equivalent to but it is not exactly identical with the original. The two equivalent H-atoms have been interchanged and the new orientation is indistinguishable from the original, because the H-atoms are equivalent and indistinguishable. A second 180° rotation will bring the molecule to the original form. Any atom which lies on the proper axis of symmetry is unshifted by any rotation about that axis. Other examples of molecules having C_2 axis are H_2S, hydrogen peroxide, cis-1,2-dichloroethylene etc.

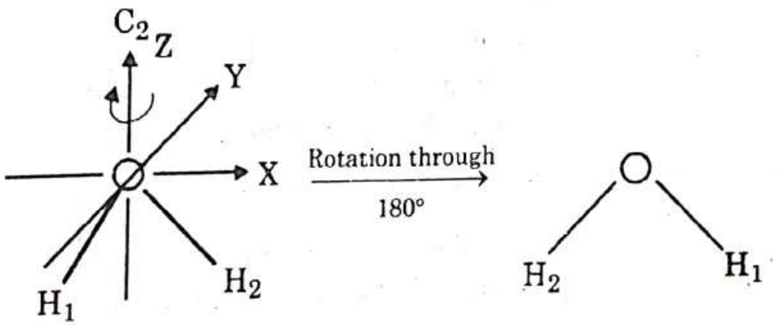


Fig. 8.2 H_2O molecule before and after C_2 operation

Figure 8.3 shows BF_3 molecule that has a three-fold axis of symmetry, C_3. Rotation about this axis by $2\pi/3$ (i.e., 120°) may be performed in a clockwise or anticlockwise direction. Either operation brings the molecule to its equivalent appearance, but neither result is identical with the original (i.e. all the atoms are not in there original places). The clockwise $\overrightarrow{C}_3$ and anticlockwise $\overleftarrow{C}_3$ rotations must therefore, be regarded as two distinct examples of rotation about a three fold axis. If however, $\overrightarrow{C}_3$ is performed twice, i.e. $\overrightarrow{C}_3^2$, the molecule is then brought into a position identical to that which results from $\overleftarrow{C}_3$ on the starting object.

$$\overrightarrow{C}_3 \times \overrightarrow{C}_3 = \overleftarrow{C}_3$$

$$(\overrightarrow{C}_3)^2 = \overleftarrow{C}_3$$

However, it may be noted that

$$\overrightarrow{C}_3^3 = E = \overleftarrow{C}_3^3$$

Thus a rotation in a clockwise manner could be expressed in terms of a rotation in an anticlockwise function or via versa.

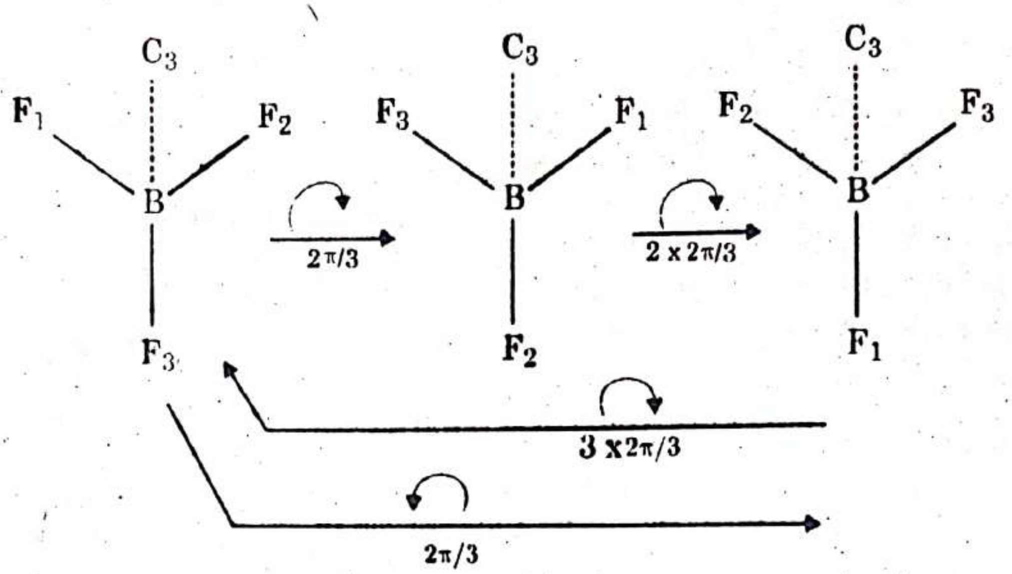


Fig. 8.3 Results of various rotation about the C_3-axis in BF_3 molecule

After discussion of above, it is easy to accept some more general statements about proper axis and proper rotation. In general an n-fold axis is denoted by C_n and a rotation by $2\pi/n$ is also represented by the symbol C_n. Rotation by $2\pi/n$ carried out successively by m times is represented by the symbol C_n^m. Also in any case $C_n^n = E$, $C_n^{m+1} = C_n$, $C_n^{m+2} = C_n^2$ and so on. The other examples of molecules having C_3 axis. are: Ammonia (NH_3), phosphine (PH_3), chloroform ($CHCl_3$), bromoform ($CHBr_3$) etc.

Fig. 8.4 shows sulfer hexafluoride (SF_6) that has fourfold axis of symmetry which passes through F_5-S-F_6 atoms and is perpendicular to the other four fluorine atoms. A rotation through $2\pi/4$ i.e., 90° about the axis is called C_4 operation. It can be seen that successive C_4-operations (all clockwise) yield four different symmetry operations, C_4, C_4^2, C_4^3 and C_4^4. Note that

$$C_4^4 = E$$

$$C_4^2 = C_2$$

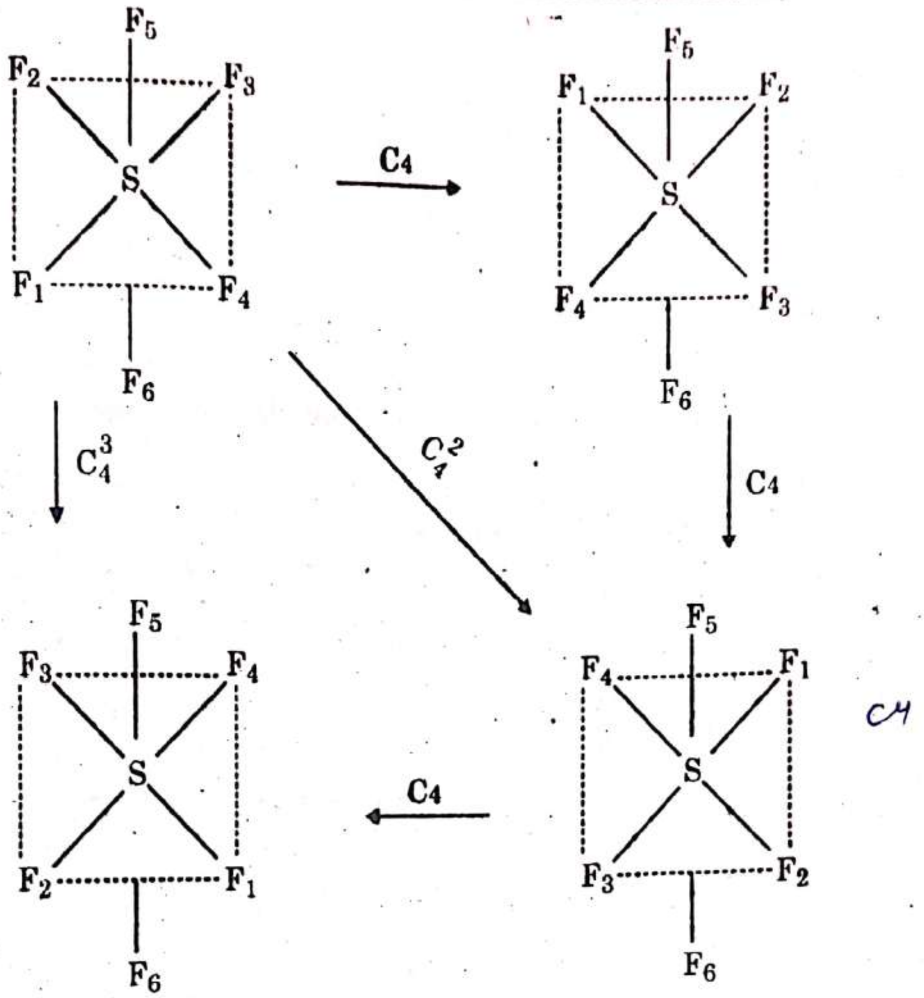


Fig. 8.4 rotation in SF_6 molecule

The fivefold and six fold axes of symmetry are seen in cyclopentadienyl anion $(C_6H_5^-)$ and benzene (C_6H_6) respectively. (Fig.8.5).

Fig.8.5 A fivefold and sixfold axes in $C_5H_5^-$ and C_6H_6.

Linear molecules such as acetylene, hydrogen chloride, etc. have an infinite-fold axis. A rotation through an indefinitely small angel θ about the internuclear axis gives rise to a conformation which is indistinguishable from the starting molecule. Such an operation which is denoted by C_α is a symmetry operation for diatomic and linear polyatomic molecules (Fig.8.6)

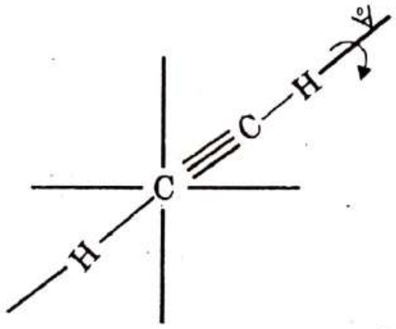


Fig.8.6 An infinite-fold axis in acetylene molecule

It should be noted here that a molecule may have, two three, four fold axes of symmetry, but the axis of n-fold notation characterized by the largest n is called the *principal axis*. This is taken along the z-axis by convention.

8.6 THE REFLECTION OPERATION AND THE MIRROR PLANE

The operation of reflection is represented by the lowercase sigma (σ), and the corresponding element is referred to as the mirror plane. Reflection in a molecule is based on mirror plane. If the molecule is left unaltered by a reflection in a plane, this plane is said to be a plane of symmetry. The results of a double reflection in the same plane is the identity operation, i.e.,

$$\sigma^2 = E$$

A reflection plane is a symmetry element that acts as a mirror and makes one half of the molecule the mirror image of the other half. If the reflection operation exists, for any point a distance r along a normal to the mirror plane there will be an equivalent point at a distance −r.

Planes of reflection are classified relative to the principal axis of rotation. If the plane contains the principle axis, the symbol is σ_v (vertical plane). If the principle axis is perpendicular to the plane of reflection, then reflection on this plane is called σ_h (horizontal plane). Besides the σ_v and σ_h planes, a special case of σ_v-plane is found in some molecules that have two-fold axes at right angles to the principal axis. If the planes of reflection bisect the angles between the two adjacent two-fold axes and pass through the principal axis, they are called σ_d planes (d for dihedral).

Figure 8.7 shows the five mirror planes found in a square plane, such as a planar MX_4 molecule. The five planes are grouped into three classes: σ_h, $2\sigma_v$ and $2\sigma_d$. Notice that all mirror planes pass through a common point at the centre of the molecule.

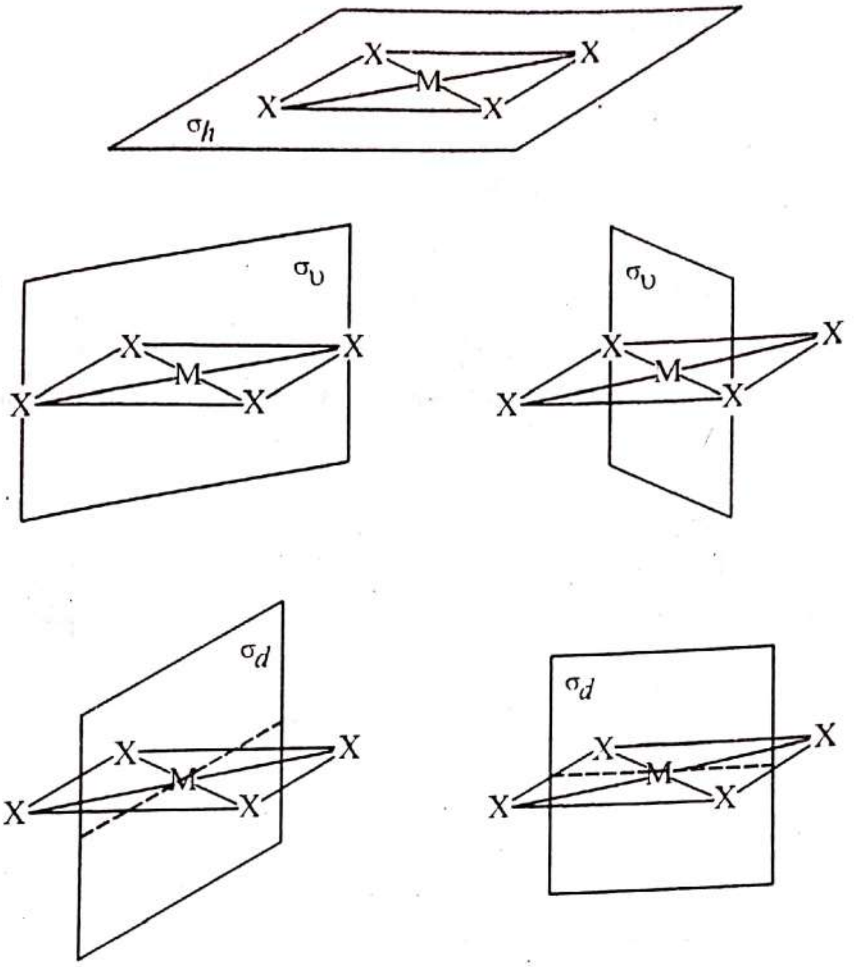


Fig. 8.7 Mirror planes of square planner molecule MX_4

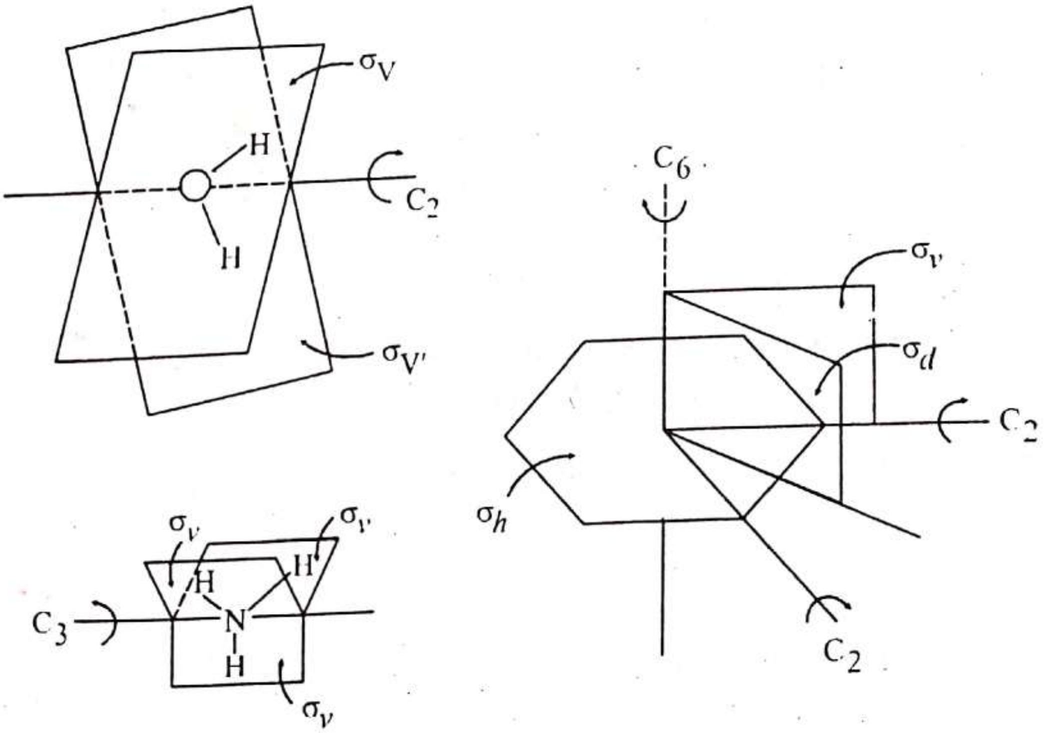


Fig. 8.8 Different reflection planes in H_2O, NH_3 and C_6H_6 molecules

Fig. 8.8 shows the different reflection planes in H_2O, ammonia and benzene molecules. It is obvious that H_2O has two σ_v and ammonia has three σ_v planes of symmetry. Benzene molecule has sixfold axis of symmetry. At right angle to the principal axis is the plane of molecule itself. A reflection in the plane of the molecule leaves the molecule unaltered. Hence benzene possesses a σ_h plane. Besides, σ_v and σ_h, benzene molecule also possess three σ_d planes.

Fig. 8.9 shows the different mirror planes in SO_3, cis-dichloroethylene, trans-dichloroethylene and ferrocene molecule. SO_3 has $3\sigma_v$ and one σ_h. Cis-dichloroethylene has $2\sigma_v$, while its transform has only σ_h. Ferrocene molecule has $5\sigma_d$ mirror planes.

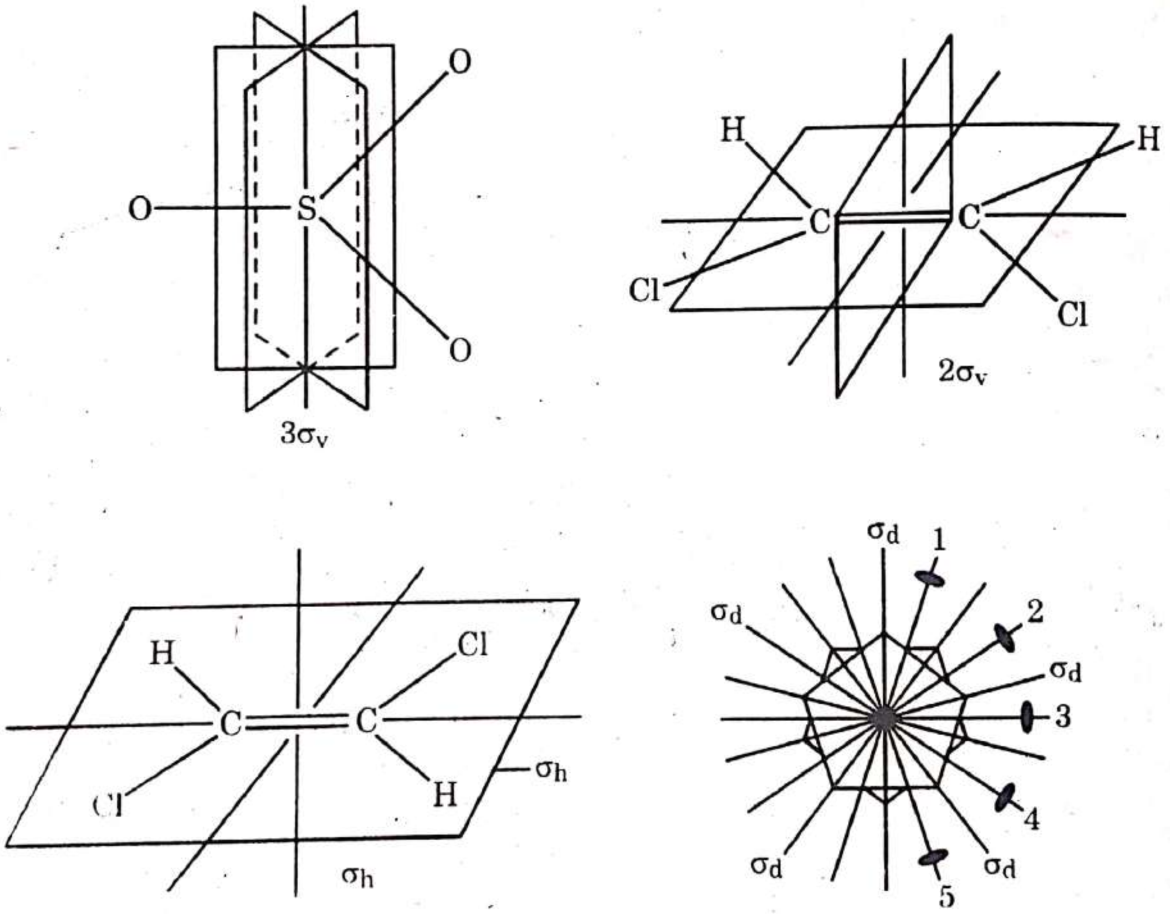


Fig. 8.9. different mirror planes in SO_3, cis-dichlorethylene, trans-dichloroethyle and ferrocene molecule.

8.7 ROTATION-REFLECTION AND THE IMPROPER AXIS

Rotation-reflection is a compound operation that consists of proper rotation by $2\pi/n$ about an axis followed by a reflection in a plane perpendicular to the axis of rotation. It is also called improper rotation and is given the symbol S_n. If σ_h is a reflection in a plane perpendicular to the principal axis, then by definition

$$S_n = C_n\sigma_h = \sigma_h C_n$$

where the order in which the operations C_n and σ_n are performed does not affect the results. One can see that this is a new form of symmetry operation. When n is even,

$$S_n^n = C_n^n \sigma_h^n = E \times E = E$$

Thus, an n-fold repetition of the improper rotation returns the molecule to its initial position. If n is odd, this

$$S_n^n = C_n^n \times \sigma_h^n = E \times \sigma_h = \sigma_h$$

An n-fold repetition would be equivalent to simple reflection in a plane perpendicular to the axis.

A tetrahedral molecule of the type XL_4 has an S_4 improper rotation, although it does not have either the C_4 or σ_h operation. This is illustrated in Fig.8.10. By comparing out a second successive S_4 operation, it can be shown that two S_4 operations are equivalent to C_2 operation.

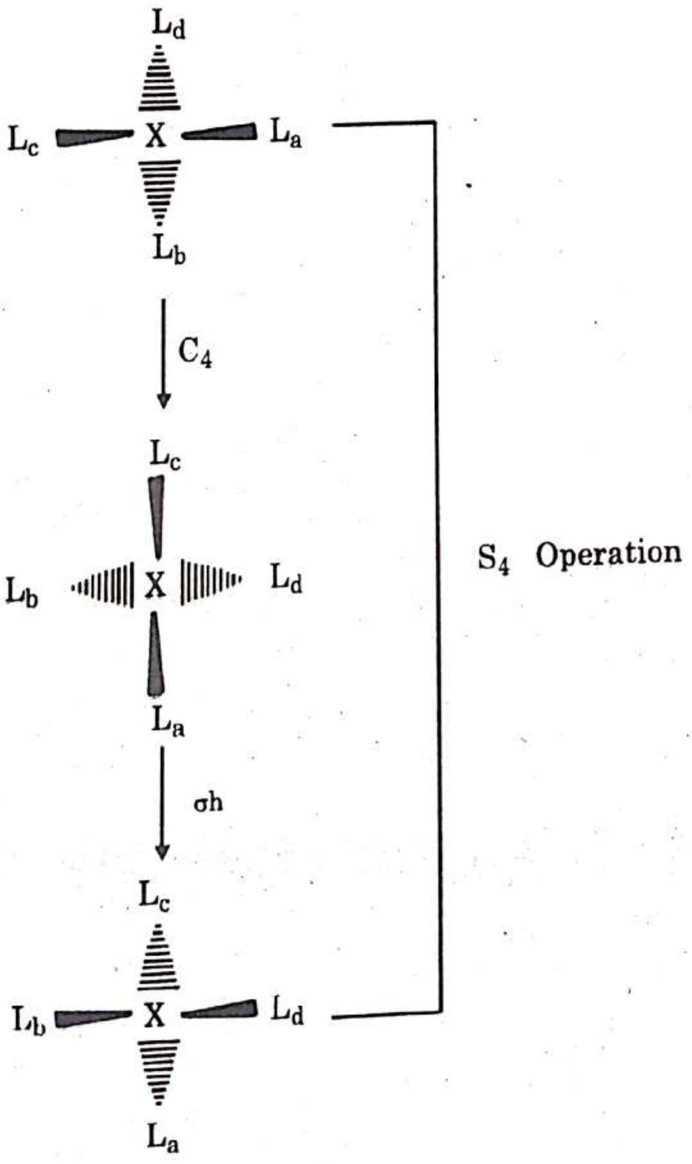


Fig.8.10 The improper rotation of a tetrahedral molecule XL_4

Methane and Allene (C_3H_4) molecules possess S_4 rotation-reflection axis. Methane molecule can be inscribed in a cubic geometry.

For methane molecule, one of the three S_4 axes may be shown as below:

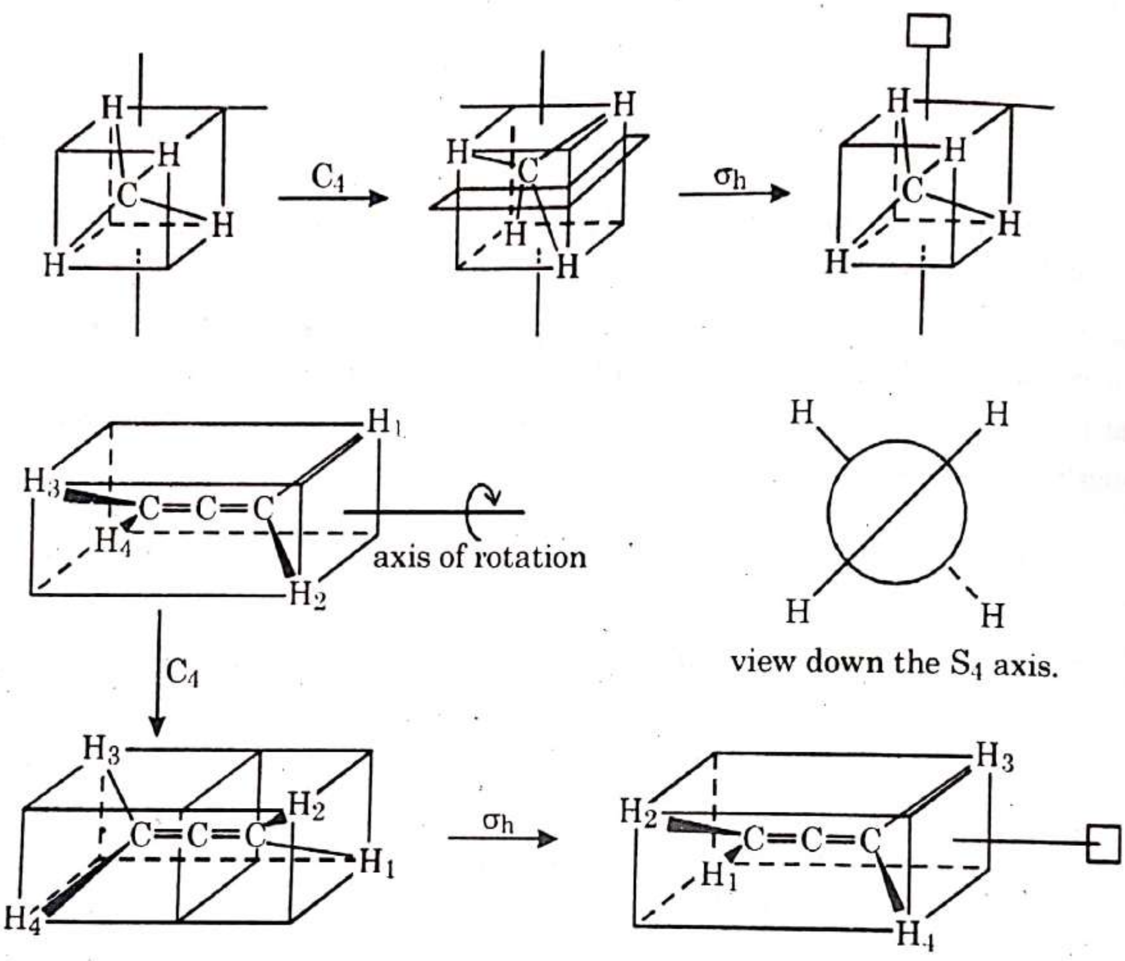


Fig. 8.11. S_4 axis of improper rotation in methane and allene molecule.

Let us consider another example of allene, C_3H_4 molecule which can be inscribed in a rectangular box. The hydrogen atoms are present at the vertices as shown in Fig. 8.11. First a rotation of $\frac{2\pi}{4} = 90°$, then reflection through a plane perpendicular to the axis of rotation results in an equivalent configuration. Hence the rotation is called S_4 improper rotation.

8.8. THE INVERSION OPERATION AND THE CENTER OF SYMMETRY

The operation of inversion is relative to the central point in the molecule through which all the symmetry elements pass. Center of the symmetry is the point such that any line drawn through it meets the same atom at equal distances in opposite direction. It can also be defined in another way. There is an inversion operation and center of symmetry if for every point in the molecule (x, y, z) there is an equivalent point at coordinates (−x, −y, −z). The central point (0, 0, 0) is referred to as the center of symmetry. It is denoted by italics *i*. Molecules that have center of symmetry are known as centrosymmetric. If the inversion operation is performed twice, it brings every point back to itself.

$$ii = i^2 = E$$

Fig. 8.11 lists the molecules with centre of symmetry. This element of symmetry is also called as S_2 axis. All homonuclear diatomic molecules possess the centre of symmetry.

$$S_2 = i;\ S_2^2 = i^2 = E$$

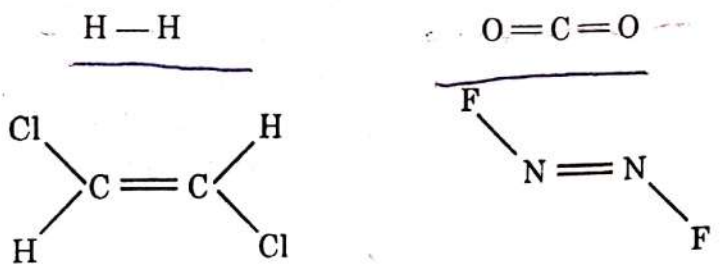


Fig. 8.11 Examples of molecules with center of symmetry.

Example 8.1

How many distinct operations are implied by a C_6 axis of rotation?

Solution

Following are the distinct operations implied by C_6 axis.

$$C_6^1 \quad C_6^2 \quad C_6^3 \quad C_6^4 \quad C_6^5 \quad C_6^6$$

$$C_3^1 \quad C_2^1 \quad C_3^2 \qquad\qquad E$$

Example 8.2

Show the effect of C_2-axis of rotation, center of symmetry, i, σ_{xz} and σ_{yz} on a point represented by the column vector (x, y, z)

Solution

$$C_2 \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} -x \\ -y \\ z \end{bmatrix}$$

$$i \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} -x \\ -y \\ -z \end{bmatrix}$$

$$\sigma_{xz} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} x \\ -y \\ z \end{bmatrix}$$

$$\sigma_{yz} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} -x \\ y \\ z \end{bmatrix}$$

8.9 THE SYMMETRY POINT GROUPS

Molecules can be classified into high symmetry molecules and low symmetry molecules, based on the symmetry elements and symmetry operations present in them. All the symmetry operations present in a molecule form a group. A molecular group is called a *point group* since all the elements of symmetry present in a molecule intersect at a common point and this point remains fixed under all the symmetry operations of the molecule. It is to be noted that the identity operation is present in all molecular points groups. The symmetry group of a molecule is denoted by a specific symbol. Molecular point groups are denoted by the symbols introduced by Schoenflies. The point group differs from the space group as is found in crystal, where some of the symmetry operations result in a translation of the molecules or a unit cell, to a new location in the crystal. The point groups for crystals are denoted by Schoenflies notation or the Hermann-Maugnin notation.

A given molecule can have a number of symmetry operations. The symmetry operations that do apply to a given molecule in its equilibrium configuration form a mathematical group. A group in mathematics consists of a set of members (which may be number or matrices) which obey the following rules.

1. Two elements of a group combine to give the third element of a group. For example, let A and B are two elements of a group, then their product (say C) will also be a member of the group

$$AB = C$$

2. An element combines with itself to form another element of the group AA = B.

3. Every group consists of one element which commutes with all the elements and leaves them unchanged. This element is known as the identity (E) element

$$EA = AE = A$$

4. Every element of the group obeys the associative law of combination. If A, B and C are the three elements of the group, then (or associative law of multiplication holds):

$$(AB)C = A(BC)$$

5. Each element of the group has an inverse or reciprocal which is also an element of the group. The element and the inverse combine to give the identity element. The inverse operation A^{-1}

$$A^{-1}A = AA^{-1} = E$$

is that which returns the object to its original position. Hence, the inverse of a C_2, σ or i operation is itself (viz., $C_2C_2 = E$; $\sigma\sigma = E$; $ii = E$). The inverse of a C_3^1 operation is a C_3^2, while the inverse of an S_4^1 operation is an S_4^3.

The set of numbers between $-\infty$ to $+\infty$ form a group by the multiplication process. It is to be noted that zero is not included as an element of the group. These numbers satisfy the rules of the group as follows:

$2 \times 4 = 8$ (by rule 1)

$2 \times 2 = 4$ (by rule 2)

$2 \times 1 = 1 \times 2$ (by rule 3)

$2 \times (4 \times 6) = (2 \times 4) \times 6 = 48$ (by rule 4)

$2 \times R = 1$, therefore $R = \frac{1}{2}$ (by rule 5)

There are different types of groups. A group in which all elements commute is called an *Abelian group*. Two elements A and B commute if AB = BA. The set of numbers between $-\infty$ and $+\infty$ form an Abelian group under the multiplication process. Zero is not included as an element of the group. In ordinary algebra, multiplication is commutative e.g.

$x \times y = y \times x$

$3 \times 6 = 6 \times 3 = 18$

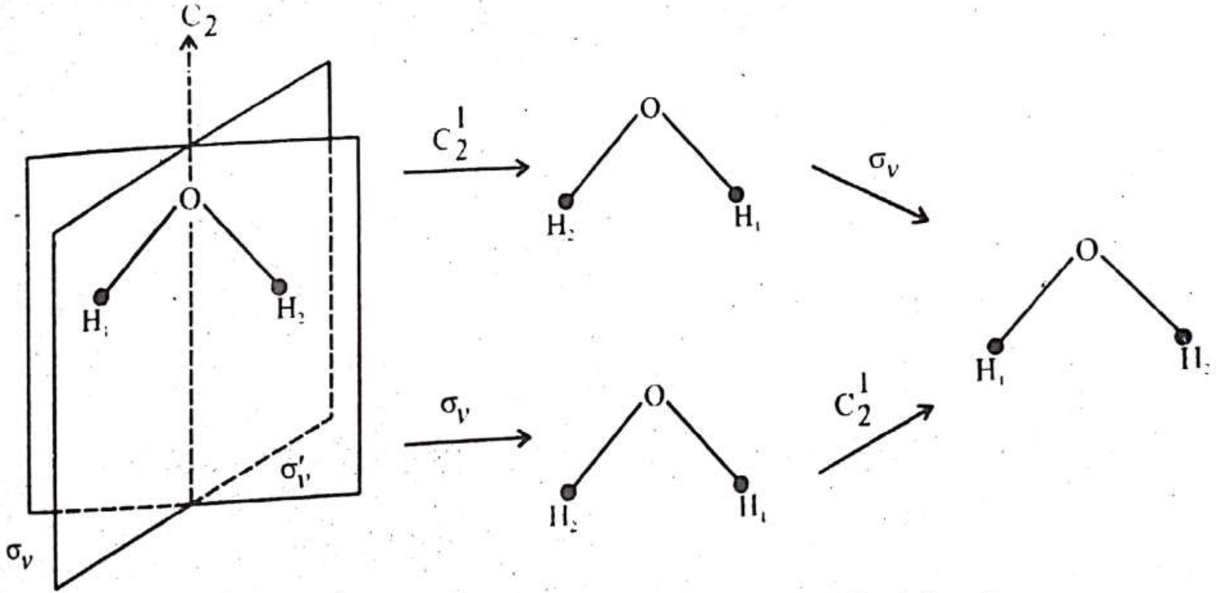


Fig.8.12 Combination of two operations in H_2O molecule

In group theory, the *commutative law* does not in general hold. Thus AB may give 'C' while BA may give 'D', where 'C' and 'D' are two more elements in the group.

The set of symmetry operations of water molecule represents an Abelian group. Fig.8.12 illustrates the idea that symmetry operations of water molecule obey the commutative law.

C_2^1 operation followed by σ_v operation leads to the configuration A. σ_v operation followed by C_2^1 leads to the same configuration as shown in fig. 8.12. The symmetry operation of water molecule satisfies the rules of the group as follows:

$C_2^1\, \sigma_v = \sigma_v'$ (by rule 1)

$C_2^1\, C_2^1 = C_2^2 = E$ (by rule 2)

$C_2^1\, E = E\, C_2^1 = C_2^1$ (by rule 3)

$C_2^1(\sigma_v, \sigma_v') = (C_2^1\, \sigma_v)\, \sigma_v' = E$ (by rule 4)

$\sigma_v \cdot \sigma_v = E$ (by rules 5)

or $\sigma_v' \cdot \sigma_v' = E$ (by rule 5)

The product operations of H_2O molecule are summarized in the following multiplication table.

Table 8.2 Multiplication Table For C_{2V} Group

		Operation A			
		E	C_2^1	σ_v	σ_v'
Operation B	E	E	C_2^1	σ_v	σ_v'
	C_2^1	C_2^1	E	σ_v'	σ_v
	σ_v	σ_v	σ_v'	E	C_2^1
	σ_v'	σ_v'	σ_v	C_2^1	E

The above table shows (since no additional operations are generated) that these four symmetry operations form a group and that the operations are commutative. The point group is designated by Schenflies symbol C_{2v}.

A group is said to be *non-Abelian* if all the elements do not commute with one another. The symmetry operations of the NH_3 molecule provide an example for the non-Abelian group. E, C_3^1, C_3^2, σ_v^1, σ_v^2 and σ_v^3 are the operation present in this molecule. The elements of this group do not obey the commutative law. Other example are AsH_3, PH_3 etc.

The number of elements in a group determine the *order of a group*. It is represented by 'h'. Any collection of the elements of a group that by themselves form a group is called a *sub-group*.

The various types of point groups are defined below and are illustrated in Table 8.2.

Point Group C_1

This group contains molecules with no elements of symmetry, except the identity (E). The identity is equivalent to a 360° rotation about any axis. HNClF, CH_3CHO and CHBrClF belong to this point group.

Point of Group C_s

This group contains molecules that only have a reflection plane σ. CH_2ClF, HOCl, Cl_2SO, pyridine etc. belong to this point group.

Point Group C_i

This group contains molecules that have only center of symmetry. Molecules like 1,2 dibromo-1,2-dichloroethane belong to this point group.

Point Group C_n

Molecules possessing only an n-fold axis of rotation belong to a C_n point group. For example, non-planar H_2O_2 belongs to C_2 point group, while propeller shaped triphenyl carbonium ion belongs to C_3 point group.

Point Groups C_{nv}

A molecule with n-fold axis of rotation and n vertical mirror planes (which are necessarily collinear with the n-fold axis) belong in one of the C_{nv} point groups. For example, H_2O, ammonia, H_2S, $XeOF_4$ etc.

Point Groups C_{nh}

Molecules with an n-fold axis and a plane of symmetry perpendicular to this axis belong to one of the C_{nh} point groups. Such a plane is referred to as horizontal mirror plane. The C_{nh} point group necessarily involves a center of symmetry as well. Transchlorethene, planar boric acid etc.

Point Groups D_n

Molecules with a C_n axis and a C_2 axis perpendicular to this axis are in the D_n point group.

Point Groups D_{nd}

Molecules with a C_n axis, a perpendicular C_2 axis and a dihedral mirror plane are in the D_{nd} point group. The dihedral mirror plane is collinear with the principal axis and bisects the two perpendicular C_2 axes.

Point Groups D_{nh}

Molecules with a C_n axis, n-vertical mirror places, nC_2 axis perpendicular to C_n axis and a horizontal mirror plane belong to one of the D_{nh} point groups if n is even, then center of symmetry is also present. Ethylene, naphthalene BF_3 belong to the point groups.

Special Point Groups

A number of molecules can be assigned to the special point groups. A linear molecule which does not have any symmetry plane perpendicular to the molecular axis belongs to the group $C_{\infty v}$, a group of infinite order consisting of rotation about the molecular axis and reflections in planes containing the molecular axis. e.g. HCl, HBr, HF molecules. Linear molecules which do have a plane of symmetry perpendicular to the molecular axis belong to another group of infinite order called $D_{\infty h}$. They also possess an infinite number of C_2 axes perpendicular to the molecular axis and an inversion center e.g. H_2, Cl_2. Br_2, N_2 etc.

The second class of special groups to be described are the so-called *cubic groups*. There are several such groups but only two be considered for our purposes. These are the groups to which regular tetrahedron and regular octahedron belong. Both of these groups may be inscribed in a cube, and hence these are also known as cubic groups.

T_d Point Group

A tetrahedron or any tetrahedral molecule possesses the following symmetry elements.

(i) Three S_4 axes coinciding with the x, y and z axes. Each of these generates the operation S_4, $S_4^2 = C_2$ and S_4^3.

(ii) Three C_2 axes coinciding with x, y and z-axes, each of which generates an operation C_2.

(iii) Four C_3 axes each of which passes through one apex and the center of opposite face. These each generate C_3 and C_3^2 operations.

(iv) Six planes of symmetry each of which generates a symmetry operation.

This entire set of operations then includes E, six improper rotation (S_4's and S_4^3's) three two fold proper rotation, eight three fold proper rotations (C_3's and C_3^2's) and six reflections, or 24 operations in all. SiF_4, CCl_4, $Ni(CO)_4$, CH_4 belong to this point group. There is no center of inversion for this point group. Thus tetrahedral molecules have E, $3C_2$, $3C_3(8C_3)$, $3S_4(6S_4)$, $6\sigma_d$.

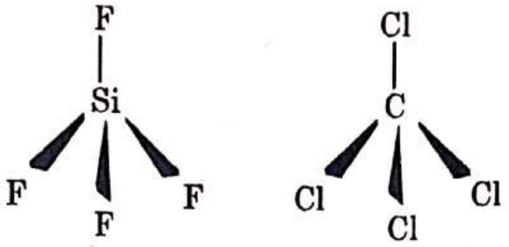


Fig. 8.13 Characteristic elements of symmetry in a regular tetrahedron.

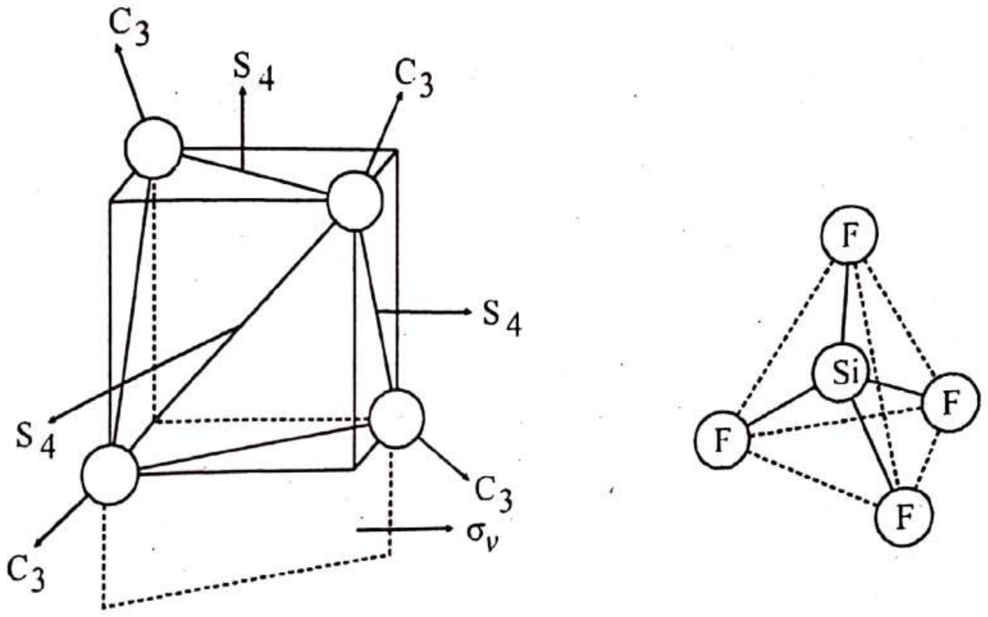


Fig. 8.14 Regular elements of symmetry in a tetrahedron

O_h Point Group

A regular octahedron has the following symmetry elements and operations.

(i) Three S_4 axes, each passing through a pair of opposite apices, each generates the operations S_4, C_2, S_4^3.

(ii) Three C_2 axes collinear with S_4's.

(iii) Three C_4 axes collinear with the S_4's and C_2's. Each generates a set of operations C_4, C_2 and C_4^3, but only C_4 and C_4^3 are new.

(iv) Four S_6 axes, each passing through the center of a pair of opposite triangular faces. Each generates a set of operations S_6, C_3, i, C_3^2, S_6^5.

(v) Six C_2' axes which bisect opposite edges. Each generates an operation C_2'.

(vi) Four C_3 axes collinear with the S_6's. Each generates two operations C_3, and C_3^2.

(vii) An inversion center which generates an operation *i* which is also generated by each of the S_6 axes.

(viii) Three planes of symmetry which pass through four of the six apices. Each generates an operation σ.

(ix) Six planes of symmetry which pass through two apices and bisect two opposite edges. Each of these generates an operation σ′.

Counting E and each of above operations, we find total of forty eight operations in this group, which is called O_h. Fig. 8.15 illustrates a regular octahedron. SF_6, AlF_6^{3-}, $PtCl_6$ belong to this point group. Thus this group has E, $8C_3$, $6C_2$, $6C_4$, $3C_2$, i, $6S_4$, $8S_6$, $3\sigma_h$, $6\sigma_d$.

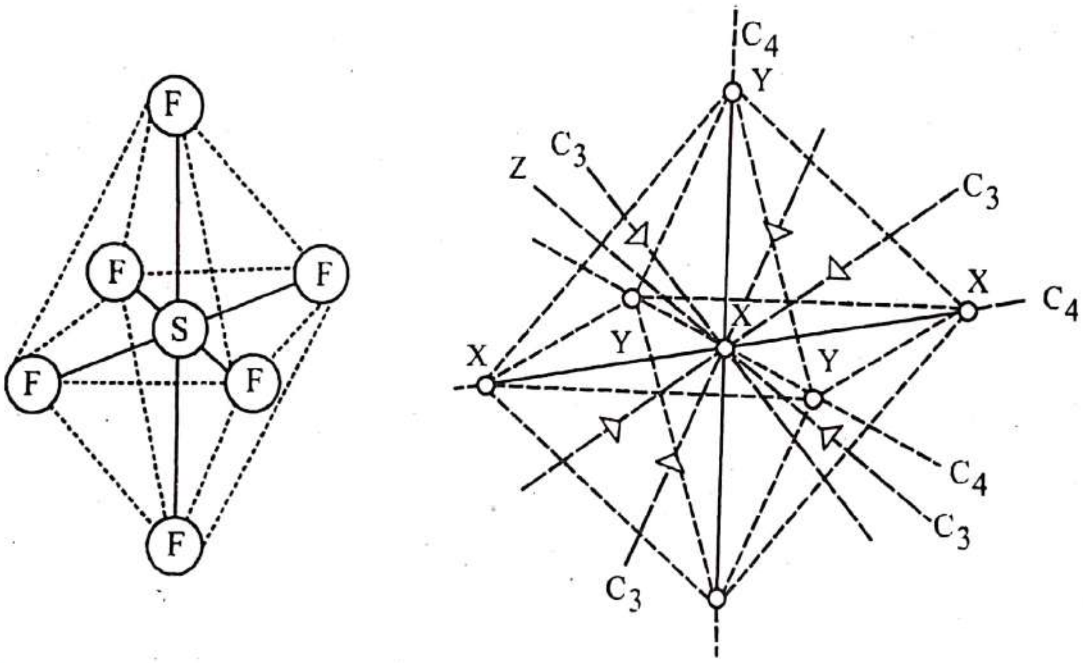


Fig.8.15 An octahedral geometry of SF_6 molecule

Table 8.3 Common Schoenflies Point Groups with Examples

Shoenflies	Symmetry Elements	Examples
C_1	E	CH_3CHO, CHClBrF
Cs	E, σ	NOCl, CH_2ClF
C_i	E, i	CH_3—CHCl—CHCl—CH_3(trans)
C_{2v}	E, C_2, $2\sigma_v$	H_2O,H_2S,CH_2Cl_2,SO_2,SO_2Cl_2
C_{3v}	E, C_3, σ_v	NH_3,PH_3,$POCl_3$,$HCCl_3$,PCl_3
C_{4v}	E, C_4, $4\sigma_v$	$XeOF_4$
$C_{\alpha v}$	E, C_∞, $\infty\ \sigma_v$	CO, HCN, OCS
C_{2h}	E, $2C_2$, σ_h, i	ClCH$=$CHCl(trans)

Shoenflies	Symmetry Elements	Examples
D_{2h}	E, $3C_2$(mutually perpendicular) $2\sigma_v$, σ_h, i	$CH_2=CH_2$, N_2O_4
D_{3h}	E, C_3, $3C_2 \perp C_3$, $3\sigma_v$, σ_h	BCl_3, PF_5
D_{4h}	E, C_4, $4C_2 \perp C_4$, $4\sigma_v$, σ_h, C_2, S_4, i	Cyclobutane, $PtCl_4^{2-}$
D_{6h}	E, C_6, $6C_2 \perp C_6$, $6\sigma_v$, σ_h, C_2, C_3, S_6 i	Benzene
$D_{\infty h}$	E, C_∞, $\alpha C_2 \perp C_\infty$, $\infty\sigma_v$, σ_h, i	H_2, CO_2, $HC\equiv CH$
D_{2d}	E, $2C_2$(mutually perpendicular) S_4, $2\sigma_d$	$H_2C=C=CH_2$ (Allene)
D_{3d}	E, C_3, $3C_2 \perp C_3$, S_6, i, $3\sigma_d$	C_6H_{12} (Cyclohexane) C_2H_6 (Staggered Ethane)

There is a systematic procedure for determining the point group of any molecule. The success of the procedure depends on your ability to find the symmetry elements present in the molecule. This skill can be achieved by continued practice. The determination of point groups may be carried out quite systematically and be facilitated by the use of decision tree as shown in Fig.8.16.

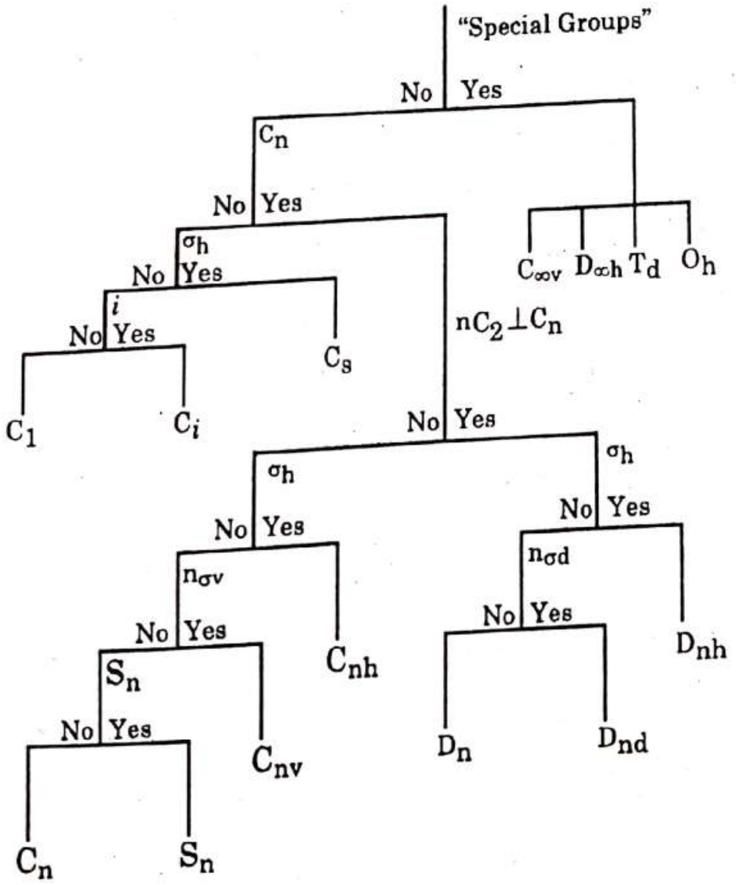


Fig.8.16 Decision tree for systematically determining the point group of a molecule

Let us be now work some examples.

Examples 8.3 H_2S

(i) H_2S is a non-linear molecule and it does not belong to any special point group like T_d, O_h and I_h.

(ii) The molecule possesses C_2 axis.

(iii) There are no C_2-axes $\perp$ to the principal axis.

(iv) There is no σ_h, so the C_{2h} group is ruled out.

(v) There are two σ_v hence the point group is C_{2v}.

Example 8.4 PCl_5

(i) PCl_5 possesses trigonal bipyramidal geometry and does not belong to any special group.

(ii) The molecule possesses C_3 principal axis.

(iii) There are three C_2 axes $\perp$ to the C_3-axis, hence it must belong to D-group.

(iv) There is a σ_h and hence the molecule belongs to D_{3h}.

Example 8.5 SF_5Cl

(i) SF_6Cl exhibits square planar bipyramidal geometry.

(ii) The molecule possess C_4 principal axis.

(iii) There are no $4C_2$ axes $\perp$ C_4 axis, here it does not belong to D-group.

(iv) There is no σ_h plane, only $4\sigma_v$ are present.

(v) Here the molecule belongs to C_{4v}.

Example 8.6 HBr

(i) HBr is a linear molecule.

(ii) It has no centre of symmetry.

(iii) It possess C_∞ as principal axis

(iv) There is no σ_h.

(v) The molecule belongs to $C_{\infty v}$.

8.10 MULTIPLICATION OF SYMMETRY OPERATORS

A molecule belonging to a particular point group possesses certain elements of symmetry. Some of the symmetry operators are inter-related by multiplication. To see how the symmetry operators are related to each other, multiplication table can be drawn for each group. For example, consider the trans-dichloroethylene molecule. It belongs to the point group C_{2h}. (operations: E, C_2, σ_h and i). It is easily seen that $C_2C_2 = C_2^2 = E$; $C_2\sigma_h = i$, $\sigma_h\, i = C_2$ and so on. All such combinations are better represented by a multiplication table in which all combinations of the type AB are shown by writing the operations A at the left of each row and B at the end of each column and AB means operation B followed by A.

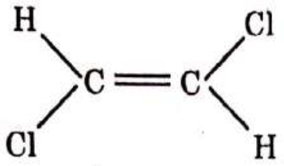


Table 8.4 Multiplication for C_{2h} Point Group

First operator / Second operator	E	C_2	σ_h	i
E	E	C_2	σ_h	i
C_2	C_2	E	i	σ_h
σ_h	σ_h	i	E	C_2
i	i	σ_h	C_2	E

The multiplication of symmetry operators is somewhat difficult to understand. Therefore the method of using a stereographic projection, for multiplication purpose, is used. For each point a stereographic projection may be drawn to show the characteristic symmetry operators. For stereographic projection one can define a working area with a dashed line and make some "general point" with a small circle as the reference point. In order to generate the point group e.g. C_{2h}, first C_2 operation is applied to the general point and then σ_h operation is carried out. The presence of a C_2 and σ_h plane, shows that there must be another symmetry operation (i.e., i) to bring the reference point to the original position. With the help of stereographic projection, we can perform multiplication as shown in Table 8.4 for trans-dichloroethylene and Table 8.5 for H_2O molecule. In the stereographic projection, the working point lies above the plane of page. Inversion through centre of the working area takes the point below the plane of page represented by x.

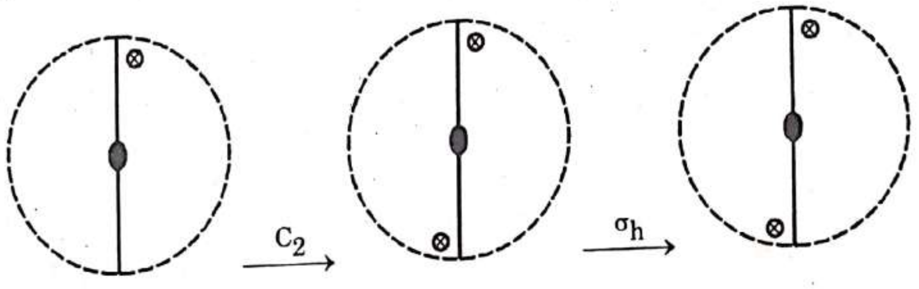


Fig.8.17 Stenographic projection for C_{2h} point group

Table 8.5 Multiplication Table for C_{2v} Point Group

First operator / Second operator	E	C_2	σ_v^{xz}	σ_v^{yz}
E	E	C_2	σ_v^{xz}	σ_v^{yz}
C_2	C_2	E	σ_v^{yz}	σ_v^{xz}
σ_v^{xz}	σ_v^{xz}	σ_v^{yz}	E	C_2
σ_v^{yz}	σ_v^{yz}	σ_v^{xz}	C_2	E

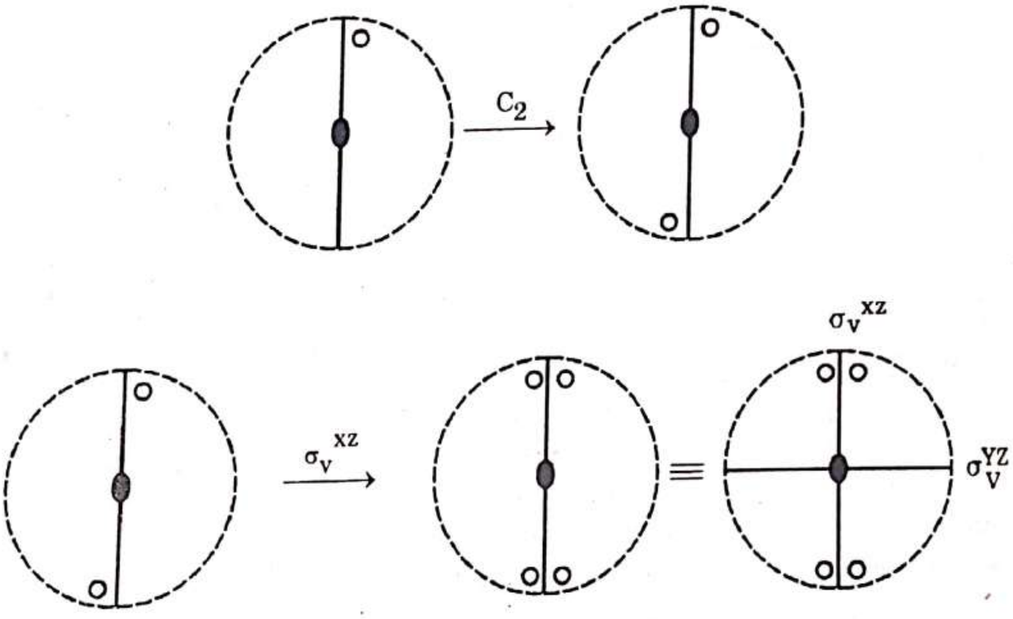


Fig.8.18 Stereographic projection for C_{2v} point group

Table 8.6 Multiplication Table for C_{3v} Point Group

First operator / Second operator	E	C_3	C_3^2	σ_v	σ_v'	σ_v''
E	E	C_3	C_3^2	σ_v	σ_v'	σ_v''
C_3	C_3	C_3^2	E	σ_v''	σ_v	σ_v'
C_3^2	C_3^2	E	C_3	σ_v'	σ_v''	σ_v
σ_v	σ_v	σ_v'	σ_v''	E	C_3	C_3^2
σ_v'	σ_v'	σ_v''	σ_v	C_3^2	E	C_3
σ_v''	σ_v''	σ_v	σ_v'	C_3	C_3^2	E

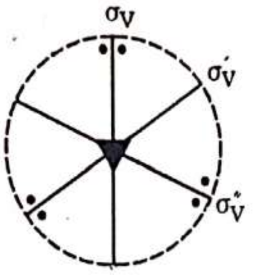


Fig. 8.19 Stereographic projection for C_{3v} point group

8.11 OPTICAL ACTIVITY AND DIPOLE MOMENTS ON THE BASIS OF POINT GROUP SYMMETRY

A knowledge of the point group symmetry of a molecule can be used to find whether the molecule is optically active or not. A molecule will be optically active if it does not possess S_n axis of any order. This means that molecule should not have the reflection plane (S_1 axis). The inversion center (S_2 axis) and any improper axis of order n. If a molecule and its mirror image cannot be superimposed, it is potentially optically active. Since a rotation followed by a reflection always converts a right-handed object into a left-handed object (i.e.) produce a mirror image of the original object), an S_n axis generates that a molecule cannot exist in separate left and right handed forms. All improper rotation axes (S_n) convert a right handed object into left handed objects, whereas all proper axis of rotation (C_n) leaves a right handed object unchanged in this respect. Hence only molecules that have no improper symmetry elements can be optically active. Thus a molecule may be chiral ,and therefore optically active, only if it does not possess an axis of improper rotation. Moreover, all molecules with center of symmetry are achiral and hence optically inactive. Some examples of optically active compounds are given in Fig.8.18.

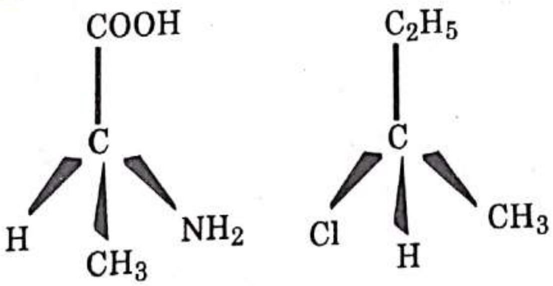
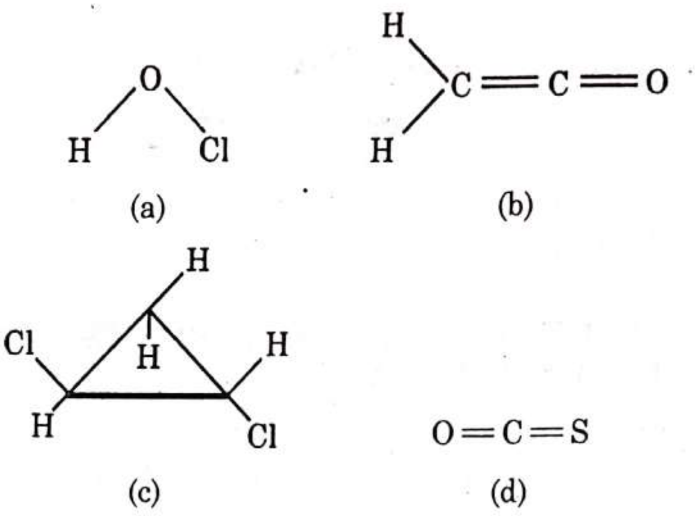


Fig.8.20 Optically active molecules with asymmetric center
(a) Alanine (b) Haloalkane

It is also possible to find out whether a molecule possess a permanent dipole or not from the point group symmetry of the molecule. A dipole moment is a vector quantity that is not affected either in direction or in magnitude by any symmetry operation of the molecule. Therefore, the dipole moment vector must be contained in each of the symmetry element. Consequently, molecules that possess dipole moments belong only to the point groups C_n, C_s and C_{nv}, or the infinite point group $C_{\alpha v}$. The dipole moment is along the C_n axis in the C_n and C_{nv} groups. In C_s group the moment lies in the reflection plane. Fig.8.19 shows molecule which possess a definite dipole moment.



(a) (b)

(c) (d)

Fig. 8.21 Examples of molecules with dipole moment (a) NOCl (C_s) (b) Ketene (C_{2v}) (c) Trans-1,2-dichlorcyclopropane (C_2) (d) COS linear ($C_{\alpha v}$)

Dipole moment of a molecule is zero if it has the inversion center. Molecules with many C_2 axes also possess zero dipole moment since they have symmetry operations which turn them upside down. The same explanation holds good for groups C_{3h}, D_{nd} and so on.

8.12 ORDER OF A GROUP

The total number of elements of a group is called *order of the group*. It is denoted by letter 'h'. The order of C_{2v} and C_{2h} point groups is four, as both groups contain four symmetry elements.

Any collection of the elements of a group that by themselves form a group is called *sub-group*. A sub-group is just a group within a group that possesses the four properties which define a group. For example, we can write E, C_2; E, σ_{xz} and E, σ_{yz} as sub-groups for the C_{2v} point group. Each sub-group is of the order 2. The order of any sub-group divided by the order of the main group gives an integer, called *index of sub-group*.

$$\text{Index of sub-group} = \frac{\text{order of sub-group}}{\text{order of the main group}}$$

For example, in C_{2v} point group

$$\text{Index of sub-group} = \frac{2}{4} = \frac{1}{2}$$

8.13 SIMILARITY TRANSFORMATION

We know that in a given group it may be possible to select various smaller sets of elements, each such set including E, however, which are in themselves groups. There is another way in which the elements of a group may be separated into smaller sets, and such sets are called *classes*. Before defining a class we must consider an operation known as *similarity transformation*.

If A and X are two elements of a group, then $X^{-1}AX$ will be equal to some element of the group, say B. We have

$$B = X^{-1}AX$$

We express this relation in words by saying that B is the *similarity transform* of A by X. We also say that A and B are *conjugate*. The following properties of conjugate elements are important.

(i) Every element is conjugate with itself. This means that if we choose any particular element, A, it must be possible to find at least one element, X, such that

$$A = X^{-1}AX$$

If we left multiply by A^{-1} we get

$$A^{-1}A = E = A^{-1}X^{-1}AX = (XA)^{-1}(AX)$$

which can hold only if A and X commute. Thus the element X may always be E, or it may be any other element which commutes with chosen element, A.

(ii) If A is conjugate with B, then B is conjugate with A. This means that if

$$A = X^{-1}BX$$

then there must be some element, Y, in the group such that

$$B = Y^{-1}AY$$

That this must be so is easily proved by carrying out appropriate multiplications, viz.,

$$XAX^{-1} = XX^{-1}BXX^{-1} = B$$

Thus, if $Y = X^{-1}$ (and this also $Y^{-1} = X$), we have

$$B = Y^{-1}AY$$

and this must be possible since any element, say X, must have an inverse, say Y.

(iii) If A is conjugate with B and C, then B and C are conjugate with each other.

3.14 CLASS OF A GROUP

A complete set of elements which are conjugate to one another is called a *class of the group*.

In order to determine the classes within any particular group we can begin with one element and work out all of its transforms using all the elements in a group, including itself, then take a second element, which is not one of those found to be conjugate to the first, and determine all its transforms, and so on until all elements in the group have been placed in one class or another. Let us start with E.

$$E^{-1}EE = EEE = E$$

$$A^{-1}EA = A^{-1}AE = E$$

$$B^{-1}EB = B^{-1}BE = E$$

Thus E must contribute by itself a class, of order 1, since it is not conjugate with any other element. This will of course be true in any group. To continue,

$$E^{-1}AE = A$$

$$A^{-1}AA = A$$

$$B^{-1}AB = C$$

$$C^{-1}AC = B$$

$$D^{-1}AB = B$$

$$F^{-1}AF = C$$

Thus the elements A, B and C are all conjugate and are therefore, members of the same class. The orders of all classes must be integral factor of the order of the group. Classes in C_{2v} point group are shown in Table 8.7.

Table 8.7. Classes of C_{2v} Point Group

Element X	$X^{-1}EX$	$X^{-1}C_2X$	$X^{-1}\sigma_{xz}X$	$X^{-1}\sigma_{yz}X$
E	E	C_2	σ_{xz}	σ_{yz}
C_2	E	C_2	σ_{xz}	σ_{yz}
σ_{xz}	E	C_2	σ_{xz}	σ_{yz}
σ_{yz}	E	C_2	σ_{xz}	σ_{yz}
	a class	a class	a class	a class

The symmetry elements of a group are put into classes. Each of the four symmetry elements of C_{2v} point group belongs to a separate class. Even the mirror planes do not belong to the same class.

8.15 MATRICES

Any symmetry operation about a symmetry element in a molecule involves the transformation of a set of coordinates x, y and z of an atom into a set of new coordinates x′, y′ and z′. The two sets of coordinates of the atom can be related by a set of equations. This set of equations may also be formulated in matrix notation. Thus each symmetry operation can be represented by a specific matrix. A knowledge of the matrices of the various operations in a molecule will be useful to solve structural problems in chemistry. For example, the symmetry of vibrational modes in molecules can be analysed using the matrices for the different operations.

A matrix is a rectangular array of numbers or symbols for numbers.

$$\begin{bmatrix} 1 & 2 & 3 \\ 4 & 5 & 6 \\ 7 & 8 & 9 \end{bmatrix} \quad \text{and} \quad \begin{bmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \\ a_{31} & a_{33} \end{bmatrix}$$

are two examples of matrices. Any elements of the matrix

$$\begin{bmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \\ a_{31} & a_{33} \end{bmatrix}$$

can be represented by a_{ij}, where i denotes the rows (horizontal sets) and j denotes the columns (vertical sets). The order or dimension of a matrix is defined by the number of rows and columns. Thus a matrix which has m rows and n columns has the dimension $m \times n$. A special case is the *square matrix* in which number of rows is equal to number of columns. The

$$\begin{bmatrix} 1 & 2 & 3 \\ 4 & 7 & 8 \\ 3 & 9 & 7 \end{bmatrix}$$

A row matrix is one which has one row and n columns. A column matrix is one which has m rows and one column. Examples of row matrix and column matrix are as follows:

Row matrix: $[1 \quad 2 \quad 4 \quad 6]$

Column matrix: $\begin{bmatrix} 1 \\ 4 \\ 6 \end{bmatrix}$

Diagonal Matrix

Consider a square matrix

$$\begin{bmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{bmatrix}$$

The elements a_{11}, a_{22} and a_{33} are called diagonal elements. The matrix is called *diagonal matrix* if all elements other than a_{11}, a_{22} and a_{33} are zero. If all the elements in a diagonal matrix are equal to 1, the matrix is referred to as *identity matrix* or *unit matrix* and is symbolized as *I*. Examples of diagonal matrix and unit matrix are given below:

Diagonal matrix: $\begin{bmatrix} 4 & 0 & 0 \\ 0 & 5 & 0 \\ 0 & 0 & 6 \end{bmatrix}$

Unit matrix: $\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$

Zero Matrix or Null Matrix

A square or rectangular matrix in which all the elements are zero is called a zero matrix or null matrix.

$$\begin{bmatrix} 0 & 0 \\ 0 & 0 \end{bmatrix}$$

is a null matrix of order 2.

Singular Martix

A singular matrix is one for which the determinant is zero. A determinant is a number which can be written in the form of an array. Example of a determinant is given below:

$$\begin{vmatrix} 3 & 7 \\ 9 & 8 \end{vmatrix}$$

The value of the determinant is

$$3 \times 8 - 9 \times 7 = -39$$

Every matrix has a value for the determinant. The matrix

$$\begin{bmatrix} 2 & 4 \\ 7 & 8 \end{bmatrix}$$

has the value −12 for the determinant. The matrix

$$\begin{bmatrix} 2 & 4 \\ 4 & 8 \end{bmatrix}$$

has the value zero for its determinant and is therefore called as a singular matrix.

Formation of Sub-matrices

Any square matrix of order n can be divided into sub-matrices as illustrated below:

$$\begin{bmatrix} 2 & 3 & 4 & 0 & 0 & 0 \\ 5 & 7 & 8 & 0 & 0 & 0 \\ 7 & 9 & 3 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 2 & 4 \\ 0 & 0 & 0 & 0 & 5 & 6 \end{bmatrix}$$

is a matrix of order 6. This matrix can be blocked into three sub-matrices. They are as follows:

$$\begin{bmatrix} 2 & 3 & 4 \\ 5 & 7 & 8 \\ 7 & 9 & 3 \end{bmatrix} \qquad [1] \qquad \begin{bmatrix} 2 & 4 \\ 5 & 6 \end{bmatrix}$$

(a) (b) (c)

Inverse of a Matrix

A square matrix B is called the inverse of A if

$$AB = BA = I$$

where I is the unit matrix. Inverse does not exist if the matrix is singular. The inverse of the matrix A

$$A = \begin{bmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{bmatrix}$$

can be obtained by using the following rules:

1. Compute the determinant of the matrix A.
2. Interchange the elements a_{11} and a_{22}.
3. Change the signs of a_{12} and a_{21}.
4. Divide each element of the matrix thus formed by the determinant of A.

The resulting matrix is the inverse of A and is represented as A^{-1}. The inverse of the matrix B

$$B = \begin{bmatrix} 3 & -2 \\ 1 & 4 \end{bmatrix}$$

is obtained as follows. The determinant of the matrix B is equal to 14. Interchange of the elements 3 and 4 leads to the matrix

$$\begin{bmatrix} 4 & -2 \\ 1 & 3 \end{bmatrix}$$

When the signs of −2 and 1 are changed, the following matrix results:

$$\begin{bmatrix} 4 & 2 \\ -1 & 3 \end{bmatrix}$$

Each element of this matrix is divided by 14 to obtain the inverse of B, B^{-1} thus obtained is given below:

$$B^{-1} = \frac{1}{14} = \begin{bmatrix} 4 & 2 \\ -1 & 3 \end{bmatrix}$$

Diagonalisation of a Matrix

The process of reducing a matrix to the diagonal matrix is referred to as diagonalisation. Let A be the square matrix of order n. P is the similarity transformation matrix which reduces A to the diagonal matrix D according to the equation

$$P^{-1}AP = D$$

Let us consider the matrix A

$$A = \begin{bmatrix} -7 & 6 \\ -18 & 14 \end{bmatrix}$$

The similarity transformation matrix P

$$P = \begin{bmatrix} 2 & 1 \\ 3 & 2 \end{bmatrix}$$

and its inverse P^{-1}

$$P^{-1} = \begin{bmatrix} 2 & -1 \\ -3 & 2 \end{bmatrix}$$

can be used to reduce A to the diagonal matrix according to the equation

$$P^{-1}AP = \begin{bmatrix} 2 & -1 \\ -3 & 2 \end{bmatrix} \times \begin{bmatrix} -7 & 6 \\ -18 & 14 \end{bmatrix} \times \begin{bmatrix} 2 & 1 \\ 3 & 2 \end{bmatrix}$$

$$= \begin{bmatrix} 2 & 0 \\ 2 & 5 \end{bmatrix}$$

Transpose of a Matrix

The transpose of a matrix is obtained by interchanging its rows and columns and is represented by $\widetilde{A}$. For example,

$$A = \begin{bmatrix} A_{11} & A_{12} & A_{13} \\ A_{21} & A_{22} & A_{23} \\ A_{31} & A_{32} & A_{33} \end{bmatrix}$$

Its transpose is

$$\tilde{A} = \begin{bmatrix} A_{11} & A_{21} & A_{31} \\ A_{12} & A_{22} & A_{32} \\ A_{13} & A_{23} & A_{33} \end{bmatrix}$$

Character of a Matrix

Let us consider an arbitrary matrix A, represented by *m* rows and *n* columns.

$$A = (A_{ij}) = \begin{bmatrix} A_{11} & A_{12} & A_{1n} \\ A_{21} & A_{22} & A_{2n} \\ \vdots & \vdots & \vdots \\ A_{m1} & A_{m2} & A_{mn} \end{bmatrix}$$

The elements on the leading diagonal of a matrix are A_{ij} (A_{11}, A_{22}, ..., A_{mn}). The sum of these elements is called the character or trace of the matrix. It is represented by symbol, χ (chi)

$$\chi(A) = \sum_i A_{ii}$$

The diagonal elements of a matrix describe how much of a function or an orbital remains in its original position after the operation.

Thus if the function (or orbital) is completely moved away, then there will be zero on the diagonal. It will not contribute to the overall character. Although the characters of a representation do not contain all the information in the matrices, they do contain the enough to make them important in the theory of group representation.

8.16 MATRIX REPRESENTATIONS OF SYMMETRY OPERATIONS

The matrices for the different symmetry operations can be obtained by considering the effect of these operations on the components of a two-dimensional vector. The results can then be extended to three dimensions.

Matrix for the Rotation Operation

Consider the vector r in the two-dimensional coordinate system shown in Fig.8.12. The vector r can be expressed as a column matrix r.

$$r = \begin{bmatrix} x \\ y \end{bmatrix} \quad (8.1)$$

x and y are the components of the vector r. Let the vector be rotated through an angel θ such that components of the vector become x′ and y′. The resulting vector r′ is expressed as another column matrix.

$$r' = \begin{bmatrix} x' \\ y' \end{bmatrix} \quad (8.2)$$

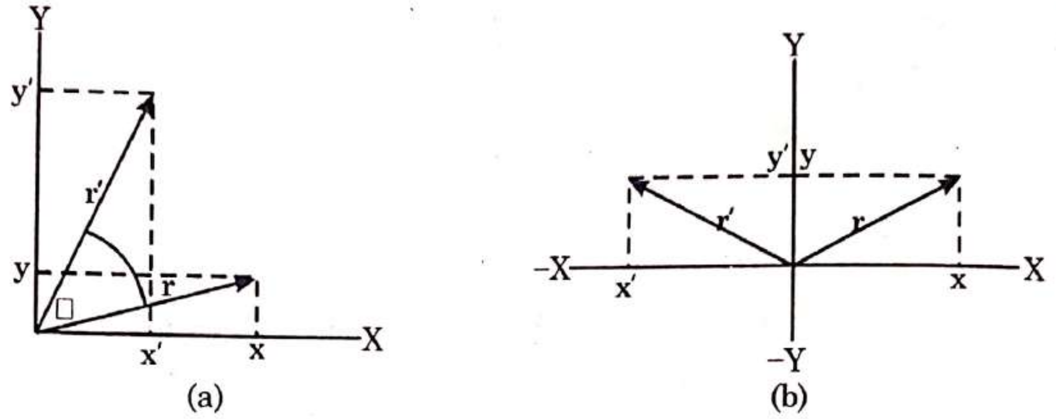


Fig. 8.12. (a) A two-dimensional coordinate system used to demonstrate the rotation of a vector through an angel θ in the xy plane (b) A two-dimensional coordinate system used to demonstrate the reflection of a vector through the Y axis.

x′ and y′ are related to x and y by the equations

$$x' = x \cos\theta + y \sin\theta \tag{8.3}$$

$$y' = -x \operatorname{sing}\theta + y \cos\theta \tag{8.4}$$

These equations are represented in the matrix form as follows:

$$\begin{bmatrix} x' \\ y' \end{bmatrix} = \begin{bmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{bmatrix} \times \begin{bmatrix} x \\ y \end{bmatrix} \tag{8.5}$$

Using Eqs. (8.1), (8.2) and (8.5) we get

$$r' = \begin{bmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{bmatrix} \times r \tag{8.6}$$

If C_n represents rotation about the axis by angel θ, then the rotation operation can be expressed symbolically as

$$r' = C_n \times r \tag{8.7}$$

From Eqs. (8.6) and (8.7) we get

$$C_n = \begin{bmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{bmatrix} \tag{8.8}$$

C_n represents the matrix for rotation operation. In three dimensions the matrix $C_n(z)$, which represents rotation about z axis, is written as

$$C_n(z) = \begin{bmatrix} \cos\theta & \sin\theta & 0 \\ -\sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix} \tag{8.9}$$

The matrices for C_3^2 operation (rotation angel θ = 240°) and C_4^1 operation (rotation angel θ = 90°) are given below:

$$C_3^2 = \begin{bmatrix} \cos 240° & \sin 240° & 0 \\ -\sin 240° & \cos 240° & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad (8.10)$$

$$C_4^1 = \begin{bmatrix} \cos 90° & \sin 90° & 0 \\ -\sin 90° & \cos 90° & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad (8.11)$$

Matrix for Reflection Operation

Consider the vector r with the components x and y. By reflection across the y axis (yz plane), the components x and y become x′ and y′. x′ and y′ are related to x and y by the equations

$$x' = -1x + 0y \quad (8.12)$$

$$y' = 0x + 1y \quad (8.13)$$

These equations are represented in matrix form as follows:

$$\begin{bmatrix} x' \\ y' \end{bmatrix} = \begin{bmatrix} -1 & 0 \\ 0 & 1 \end{bmatrix} \times \begin{bmatrix} x \\ y \end{bmatrix} \quad (8.14)$$

Equation (8.14) is alternatively represented by

$$r' = \begin{bmatrix} -1 & 0 \\ 0 & 1 \end{bmatrix} \times r \quad (8.15)$$

The reflection operation is expressed symbolically as

$$r' = \sigma_{yz} \times r \quad (8.16)$$

From Eqs. (8.15) and (8.16) we get

$$\sigma_{yz} = \begin{bmatrix} -1 & 0 \\ 0 & 1 \end{bmatrix}$$

Extending to three dimensions we get

$$\sigma_{yz} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Matrix for Improper Rotation about the S_n Axis

The matrix for improper rotation is given by the product of $C_n(z)$ matrix and σ_{xy}. Thus the matrix S, which represents improper rotation about the z axis, is written as

$$S = \begin{bmatrix} \cos\theta & \sin\theta & 0 \\ -\sin\theta & \cos\theta & 0 \\ 0 & 0 & +1 \end{bmatrix} \times \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

$$S = \begin{bmatrix} \cos\theta & \sin\theta & 0 \\ -\sin\theta & \cos\theta & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

The matrix for S_3^2 operation is given below:

$$S_3^2 = \begin{bmatrix} \cos 240^\circ & \sin 240^\circ & 0 \\ -\sin 240^\circ & \cos 240^\circ & 0 \\ 0 & 0 & -1 \end{bmatrix} \quad (8.17)$$

Matrix for Inversion Operation

The x, y and z components of a vector r are transformed into their respective negatives by the inversion operation. The components x, y and z are related to –x, –y and –z by the equations

$$i \,.\, x = -1x + 0y + 0z \quad (8.18)$$

$$i \,.\, y = 0x - 1y + 0z \quad (8.19)$$

$$i \,.\, z = 0x + 0y - 1z \quad (8.20)$$

where $i \,.\, x$, $i \,.\, y$ and $i \,.\, z$ refer to inversion operation on the components x, y and z. In matrix form, these equations become

$$i \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \times \begin{bmatrix} x \\ y \\ z \end{bmatrix} \quad (8.21)$$

From this equation we get the matrix for inversion i as

$$i = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \quad (8.22)$$

Matrix for Identity Operation

By identity operation the components x, y and z of a vector remain unchanged. The equations which represent the effect of identity operation on the vector r are given below:

$$E \,.\, x = 1x + 0y + 0z \quad (8.23)$$

$$E \,.\, y = 0x + 1y + 0z \quad (8.24)$$

$$E \,.\, z = 0x + 0y + 1z \quad (8.25)$$

E . x, E . y and E . z in these equations refer to the identity operation on the components x, y and z. In matrix from, these equations become

$$E\begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \times \begin{bmatrix} x \\ y \\ z \end{bmatrix} \qquad (8.26)$$

From this equation we get the matrix for identity operation E as

$$E = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \qquad (8.27)$$

The sum of the diagonal elements of a square matrix is called the *trace* or *character of the matrix*. The characters of the various matrices corresponding to the symmetry operations are listed in Table 8.8.

Table 8.7

Symmetry Operation	Character of Matrix
Identity	3
Rotation	$2\cos\theta^* + 1$
Inversion	-3
Improper rotation	$2\cos\theta - 1$
Reflection	1

* θ refers to the angel of rotation about the axis.

8.17 SYMMETRY PROPERTIES OF ATOMIC ORBITALS

Let us now consider the effect of symmetry operators (characteristic for a molecule) on the atomic and molecular orbitals. Consider the 2s and 2p atomic orbitals of oxygen in water molecule having C_{2v} symmetry. The operators are: E, C_2, σ_v^{xz} and σ_v^{yz}. The operator E leaves everything unchanged. The 2s orbital of oxygen has spherical symmetry and it will not altered by rotation and reflections. The effect of other operations on the three 2p orbitals is shown in the following figure:

no change = +1

change = −1

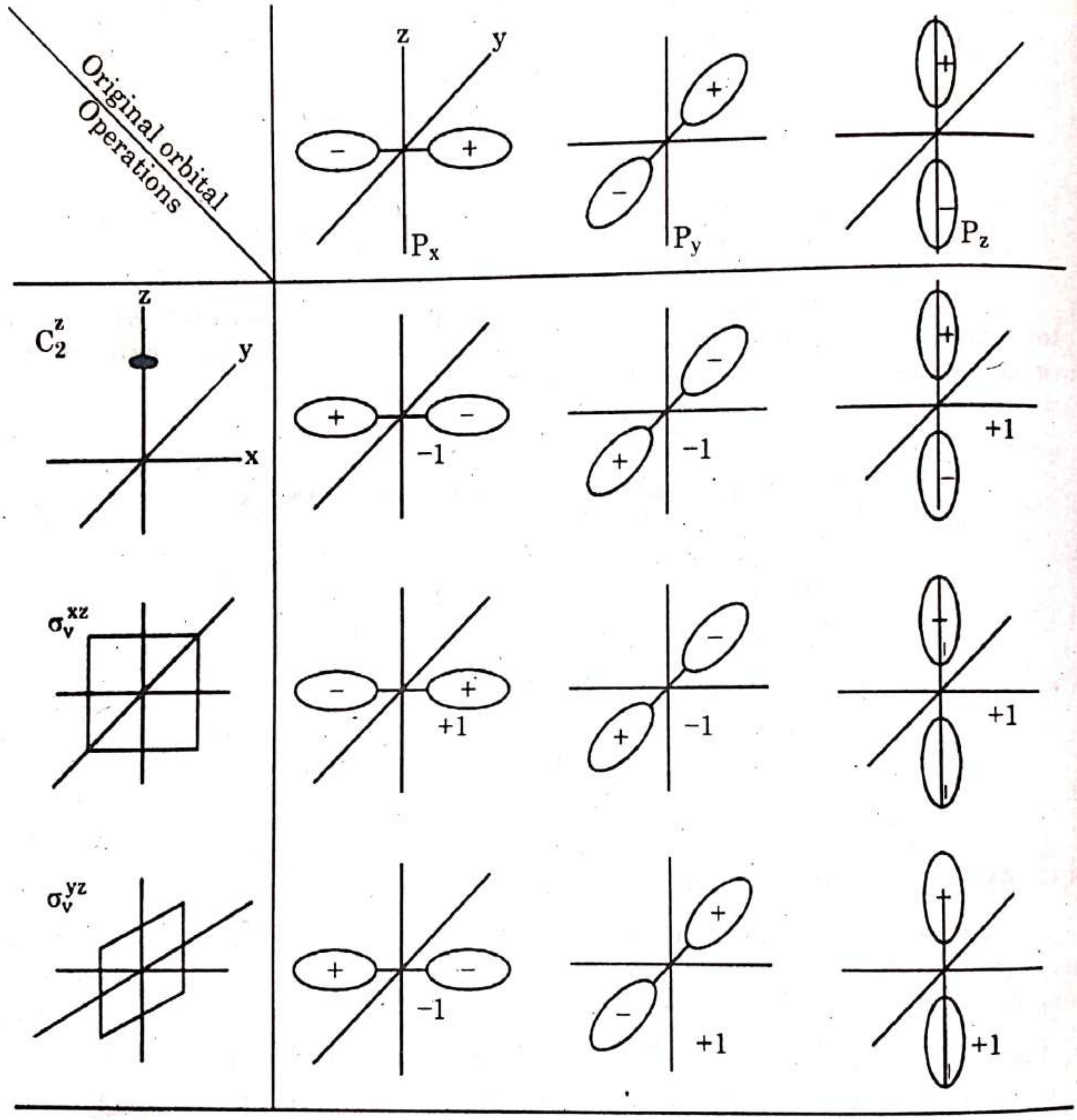


Fig. 8.13. The effect of C_2, $\sigma_v{}^{xz}$, $\sigma_v{}^{yz}$ operators on the three p orbitals.

It may be seen that each symmetry operation either restores the original positions or there is a change in sign. When an operator generates a new orbital identical in sign and position with the original, the effect of the operator is the same as multiplying the original orbital by +1. On the other hand when the operator restores the oribital to its original position with a change of sign, the effect is the same as if multiplied by −1. These +1 and −1 numbers are matrices which represent the action of an operator.

The effect of C_{2v} point group operators on oxygen orbitals can be summarized by tabulating the representative matrices as shown in Table 8.9.

Table 8.9. Effect of C_{2v} point group operation on oxygen orbitals.

Orbitals	E	C_2	σ_v^{xz}	σ_v^{yz}	
2s	+1	+1	+1	+1	Γ_1
$2p_x$	+1	−1	+1	−1	Γ_2
$2p_y$	+1	−1	−1	+1	Γ_3
$2p_z$	+1	+1	+1	+1	Γ_1

It is obvious that the product of any two symmetry operators is equivalent to multiplications of their matrices. The collection of matrices representing the effect of symmetry operators of a group is called a representation of that group. It is represented by the symbol, Γ. A representation may be checked as faithful if their multiplications correspond to the operators of the point group,. Let us think of a representation and see if it is a true representation e.g.

	E	C_2	σ_v^{xz}	σ_v^{yz}
Γ′	+1	−1	−1	−1

Table 8.10

Symmetry Operators	Γ_1	Γ_2	Γ_3	Γ′
$EC_2 = C_2$	$+1 \times +1 = +1$	$+1 \times -1 = -1$	$+1 \times -1 = -1$	$+1 \times -1 = -1$
$E\sigma_v^{xz} = \sigma_v^{xz}$	$+1 \times +1 = +1$	$+1 \times +1 = +1$	$+1 \times -1 = -1$	$+1 \times -1 = -1$
$E\sigma_v^{yz} = \sigma_v^{yz}$	$+1 \times +1 = +1$	$+1 \times -1 = -1$	$+1 \times +1 = +1$	$+1 \times -1 = -1$
$C_2\sigma_v^{xz} = \sigma_v^{yz}$	$+1 \times +1 = +1$	$-1 \times +1 = -1$	$-1 \times -1 = +1$	$-1 \times -1 = +1$
$C_2\sigma_v^{yz} = \sigma_v^{xz}$	$+1 \times +1 = +1$	$-1 \times -1 = +1$	$-1 \times +1 = -1$	$-1 \times -1 = +1$
$\sigma_v^{xz}\sigma_v^{yz} = C_2$	$+1 \times +1 = +1$	$+1 \times -1 = -1$	$-1 \times +1 = -1$	$-1 \times -1 = +1$

The for the C_{2v} point group, Γ_1, Γ_2 and Γ_3 are faithful representations for the symmetry operators whereas Γ′ is not a faithful representation.

8.18 REDUCIBLE AND IRREDUCIBLE REPRESENTATIONS

We have seen several examples of products operation in connection with Table 8.2. These products and the effects of these operations on a point in a molecule can be given an actual algebraic significance by writing the symmetry operations as matrices. When these matrices are multiplied by each other the results are the same as when operations are multiplied by each other, as shown in Table 8.2. Therefore, these matrices are referred to as *representatives* of their respective operations in the point group. The group multiplication table can be reproduced by matrix multiplications of matrix representatives. The set of matrices for the various symmetry operations of a point group forms a *representation.*

Let us consider the C_{2v} point group as an example E, C_2, σ_v^{xz} and σ_v^{yz} are the four symmetry operations present in this group. The matrix representation for this point group is given below:

$$E = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \qquad C_2 = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$\sigma_v^{xz} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \qquad \sigma_v^{yz} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Multiply the transformation matrix for C_2 by the transformation matrix for σ_v^{xz} and identify the operation that corresponds with the product.

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Thus the product yield the transformation matrix for σ_v^{yz} so that

$$\sigma_v^{xz} C_2 = \sigma_v^{yz}$$

as shown in Table 8.2.

Thus any set of numbers of matrices that have the same multiplication table as the operations in the group form the representation of the group. There are an infinite number of such representations of a group, but there are a finite number that are, in a mathematical sense, more fundamental than the others. Representations can be divided into two types.

1. Reducible Representation

Representation of a group consists of a set of matrices each of which corresponds to a symmetry element in a group and these matrices combine in the same way as the symmetry elements do. If it is possible to simplify a matrix representation by performing the same similarity transformation as each of the matrices so that they are all reduced to the same block diagonalized form. The original representation is then said to be *reducible.* In the reduction of representation, the block diagonal form for all the matrices corresponding to the symmetry operations of the group should be same.

Let A, B, C be the matrices which form representation of a group and X be the similarity transformation matrix of this group such that

$$X^{-1}AX = A'$$

$$X^{-1}BX = B'$$

$$X^{-1}CX = C'$$

Then if X is the proper transformation matrix, we have

$$A' = \begin{bmatrix} a_1' & 0 & 0 & 0 \\ 0 & a_2' & 0 & 0 \\ 0 & 0 & a_3' & 0 \\ 0 & 0 & 0 & a_4' \end{bmatrix} \quad \text{or} \quad B' = \begin{bmatrix} b_1' & 0 & 0 & 0 \\ 0 & b_2' & 0 & 0 \\ 0 & 0 & b_3' & 0 \\ 0 & 0 & 0 & b_4' \end{bmatrix}$$

The new matrix A′(or B′) is now blocked out along the diagonal into smaller matrices a_1', a_2', a_3', a_4' (or b_1', b_2', b_3', b_4') etc. with the off diagonal elements equal to zero. Thus a given set of matrices form a reducible representation.

2. Irreducible Representation

If it is not possible to find a similarity transformation matrix which will reduce the matrices of representation Γ, then the representation is said to be *irreducible*. All one-dimensional representations are always irreducible. The example of an irreducible representation is illustrated below:

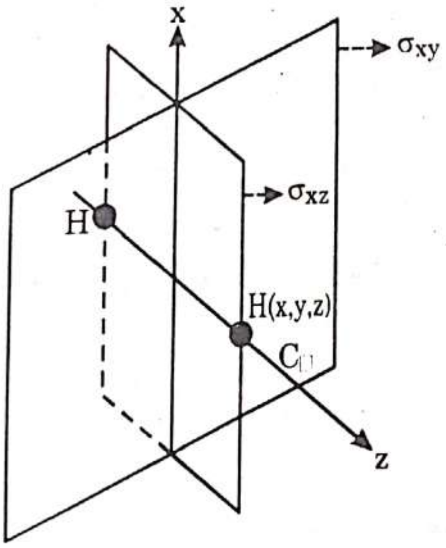


Fig. 8.14. The C_∞ axis, vertical plane and horizontal plane in H_2 molecule.

Consider the matrices of transformation for the z-coordinate of a hydrogen atom in hydrogen molecules, which result by the symmetry operations of $D_{\infty h}$ group. The operations of $D_{\infty h}$ group are E, C_∞, σ_v, C_2, σ_h, S_∞ and *i*. It is seen from Fig. 8.14 that the z-coordinate is unaffected by E, C_∞ and σ_v operations. The equations and matrices for the transformation of z-coordinate of hydrogen atom by these operations are given below:

$E\,.\,z = 1z$

E matrix = [1]

$C_\infty\, z = 1z$

C_∞ matrix = [1]

$\sigma_v\,.\,z = 1z$

σ_v matrix = [1]

All the other operations of this group change the coordinate z of hydrogen atom into −z and we get the following equations and matrices for the transformation.

$C_2\,.\,z = -1z$ $\qquad$ C_2 matrix = [−1]

$S_\infty\,.\,z = -1z$ $\qquad$ S_∞ matrix = [−1]

$\sigma_h\,.\,z = -1z$ $\qquad$ σ_h matrix = [−1]

$i\,.\,z = -1z$ $\qquad$ i matrix = [−1]

The matrix representation thus obtained for the z-coordinate of the hydrogen atom in the hydrogen molecule is given below:

	E	C_∞	σ_v	C_2	S_∞	σ_h	i
Γ	[1]	[1]	[1]	[−1]	[−1]	[−1]	[−1]

Reducible representations and irreducible representations play a major role in the application of group theory to solve problem in chemistry. The first step in any application of group theory involves the formation of the reducible representation. This representation is then decomposed into the various irreducible representations of the point group under consideration.

8.19 GENERATION OF AN IRREDUCIBLE REPRESENTATION

We have been discussing representations of a point group but have not yet discussed how to find them. For this, we require to know what effect a symmetry operation produces on the set of coordinates (x, y, z) of a point, or a function of coordinates, which we call *basis* of representation.

(i) Cartesian Coordinates as Bases

Consider a molecule belonging to C_{2h} point group and concentrate on the effect of the four symmetry operation E, C_2, σ_h and i on the coordinates of atom 1 (Fig. 8.15).

Let z-axis be the C_2 axis of symmetry; then the effect on z coordinate of the atom 1 can be expressed as,

$$E(z) = z,\ \ C_2(z) = z,\ \ \sigma_h = -z,\ \ i(z) = -z$$

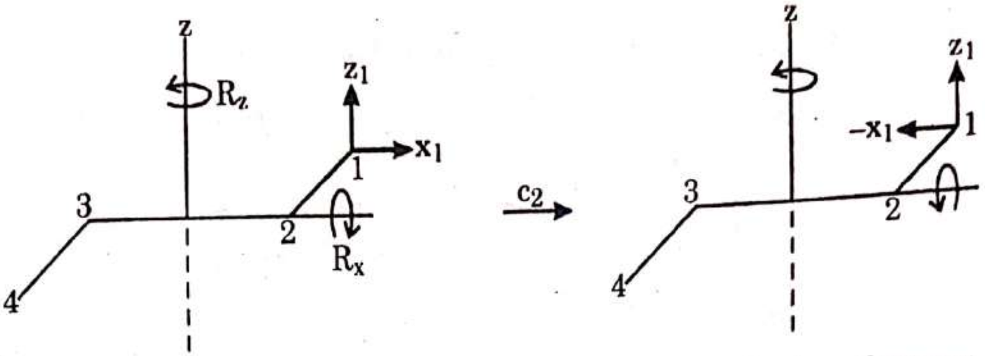


Fig. 8.15. Effect of symmetry operations on the coordinates of atoms; only x and z axes have been shown in the figure.

that is, the z coordinate is symmetric with respect ot E, and C_2, but is antisymmetric with respect to σ_h and i. This generates the following representation.

E	C_2	σ_h	i	Basis
1	1	−1	−1	(z)

Similarly, the effect on the x and y coordinates of the same atom 1 can be seen to be as follows.

$E(x) = x,\quad C_2(x) = -x,\quad \sigma_h(x) = x,\quad i(x) = -x$

$E(y) = y,\quad C_2(y) = -y,\quad \sigma_h(y) = y,\quad i(y) = -y$

Accordingly, both x and y generate the same representation,

E	C_2	σ_h	i	Basis
1	−1	1	−1	(x or y)

(ii) Rotational Coordinate as Bases

Rotations R_x, R_y and R_z around these Cartesian axes can also act as bases. This basis set can be conveniently understood by using curved arrows, e.g. an arrow around x-axis to represent R_x, etc. (Fig. 8.15). It requires a little imagination to see the effects of E, C_2, σ_h and i on the curved arrows. If you stand before a plane mirror and rotate your finger around the vertical (z) axis, the direction of the rotation of the image in the mirror is unchanged, but if you rotate it around the horizontal axis (x), the direction of rotation in the mirror is reversed.

The effects of E, C_2, σ_h and i on R_x, R_y and R_z can be seen to be as follows:

$E(R_x) = R_x,\quad C_2(R_x) = -R_x,\quad \sigma_h(R_x) = -R_x,\quad i(R_x) = R_x$

$E(R_y) = R_y,\quad C_2(R_y) = -R_y,\quad \sigma_h(R_y) = -R_y,\quad i(R_y) = R_y$

$E(R_z) = R_z,\quad C_2(R_z) = -R_z,\quad \sigma_h(R_z) = -R_z,\quad i(R_z) = R_z$

The following representations are generated accordingly:

C_{2h}	E	C_2	σ_h	*i*	Basis
	1	1	1	1	R_z
	1	–1	–1	1	(R_x, R_y)

We have thus generated a total four representations for C_{2h} group which are shown in Table 8.11.

Table 8.11. Representation of C_{2h} point group.

C_{2h}	E	C_2	σ_h	*i*	Basis
1	1	1	1	1	R_z
2	1	–1	–1	1	R_x, R_y
3	1	–1	1	–1	x, y
4	1	1	–1	–1	z

The following important features of these representations are to be noted:

(i) A single coordinate is sufficient to act as a basis for a single representation.

(ii) Each representation is irreducible, consisting of numbers ±1 (or the 1 × 1 matrices)

(iii) The numbers ±1 actually represent the "characters" of transformation of the coordinates under the symmetry operations, e.g.

$$C_2(z) = z \quad \text{and} \quad C_2(x) = -x$$

mean that z is symmetric and x antisymmetric to transformation under the operation C_2.

(iv) A total of only four irreducible representations can be generated for C_{2h} group.

(v) There is one representation (Γ) which is symmetric to transformation under all operations (i.e., totally symmetric).

Irreducible representations of dimensions greater than one are generated for groups having principal axis C_n with $n > 2$. The C_n axis is taken as the z-axis (vertical) and the rotation considered in xy plane. A rotation about C_n axis leaves the z-coordinate of a point unchanged (symmetric) but the x and y coordinates are neither unchanged nor just revised in sign; the effect is a mixing of the two coordinates.

8.20 GENERATION OF REPRODUCIBLE REPRESENTATION

We have seen that irreducible representations are generated for a point group by using a single coordinate (as in C_{2h} group) or a pair of coordinates x and y (as in C_{3v}, C_{4v}, etc.) as the basis. If we use the set of all the coordinates of an atom, we generate a representation consisting of larger matrices which are reducible to small irreducible matrices. For example, take the case of C_{2h} group. using x, y z collectively as a basis, written a 3 × 1 matrix, we get,

$$E\begin{bmatrix}x\\y\\z\end{bmatrix}=\begin{bmatrix}x\\y\\z\end{bmatrix}=\begin{bmatrix}1&0&0\\0&1&0\\0&0&1\end{bmatrix}\begin{bmatrix}x\\y\\z\end{bmatrix}$$

$$C_2\begin{bmatrix}x\\y\\z\end{bmatrix}=\begin{bmatrix}x\\y\\z\end{bmatrix}=\begin{bmatrix}-1&0&0\\0&-1&0\\0&0&1\end{bmatrix}\begin{bmatrix}x\\y\\z\end{bmatrix}$$

$$\sigma_h\begin{bmatrix}x\\y\\z\end{bmatrix}=\begin{bmatrix}x\\y\\-z\end{bmatrix}=\begin{bmatrix}1&0&0\\0&1&0\\0&0&-1\end{bmatrix}\begin{bmatrix}x\\y\\z\end{bmatrix}$$

$$i\begin{bmatrix}x\\y\\z\end{bmatrix}=\begin{bmatrix}-x\\-y\\-z\end{bmatrix}=\begin{bmatrix}-1&0&0\\0&-1&0\\0&0&-1\end{bmatrix}\begin{bmatrix}x\\y\\z\end{bmatrix}$$

A three-dimensional representation Γ^1 for C_{2h} group is generated accordingly. However, in Γ^1 all the 3-dimensional matrices are diagonal and each is reducible to three 1 × 1 matrices.

Labelling the Representations

Instead of using the symbol Γ, it is customary to use letters A, B, E, F, etc., to label the irreducible representation.

The letters A and B are reserved for one-dimensional representations, E for 2-dimensional, F for 3-dimensionl, etc. The character of the identity operation (E) is equal to the dimension of the representation. (The reader should be cautious of the use of letter E, E is used for identity and also for two dimensional representation.)

A totally symmetric representation is given the symbol A_1. But if the point group contains the operation i, the total symmetry is indicated by A_{1g}.

If in the one-dimensional representation $\chi(C_n) = +1$, the representation is A and if $\chi(C_n) = -1$, it is B.

The subscript 1 or 2 is attached to the labels A and B to denote whether $\chi(\sigma_v) = +1$ or -1 respectively; σ_v may be any symmetry plane containing C_n.

To indicate in a representation whether $\chi(\sigma_h) = +1$ or -1, single prime (′) or a double prime (″) is used.

The subscript g or u is used according to whether $\chi(i) = +1$ or -1 respectively.

8.21 CHARACTER TABLES FOR POINT GROUPS

Reducible representations and irreducible representations play a major role in obtaining solutions to problems of hybridization, molecular vibrations, delocalization energies of π-electron systems and so on. In all these applications, the first step involves point group determination and formation of the reducible representation. The characters of the matrices in the reducible representation are used to split it into the different irreducible representations of the group. Every point group consists of a certain number of irreducible representations.

It has been reported that for almost all the applications of group theory we do not need the complete matrices, only sum of the diagonal elements. The sum of the diagonal elements of a matrix is called its *character*. The list of characters of all the possible irreducible representations of a group is called the *character table*. Each group is represented by a character table which is a "condensate" of its properties.

Character tables play a vital role in solving problems such as molecular vibrations. The character table for a point group can be constructed with the knowledge of properties of irreducible representations. The properties of irreducible representations can be obtained from orthogonality theorem.

As examples, the character tables for C_{2v}, C_{2h} and C_{3v} point groups are shown below.

Table 8.12. The Character table for C_{2v} point group.

C_{2v}	E	C_2	σ_v^{xz}	σ_v^{yz}		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	−1	−1	R_z	xy
B_1	1	−1	1	−1	x, R_y	xz
B_2	1	−1	−1	1	y, R_x	yz

Table 8.13. Character Table for C_{2h} point group.

C_{2h}	E	C_2	*i*	σ_h		
A_g	1	1	1	1	R_z	x^2, y^2, z^2, xy
B_g	1	−1	1	−1	R_x, R_y	xz, yz
A_u	1	1	−1	−1	z	
B_u	1	−1	−1	1	x, y	

Table 8.14. Character table for C_{3v} point group.

C_{3v}	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	z	$x^2 + y^2, z^2$
A_2	1	1	–1	R_z	
E	2	–1	0	(x, y) (R_x, R_y)	$(x^2 - y^2, xy)$ (xz, yz)

Table 8.15. Character table for tetrahedral point group.

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$		
A_1	1	1	1	1	1		
A_2	1	1	1	–1	–1		
E	2	–1	2	0	0		$(2z^2 - x^2 - y^2, x^2 - y^2)$
T_1	3	0	–1	1	–1	(R_x, R_y, R_z)	
T_2	3	0	–1	–1	1	(x, y, z)	(xy, xz, yz)

It is obvious that each character table is divided into four sections. In the upper left column is the Schocnflies symbol for the group. The first column shows the types of representation (names of irreducible representations). Mulliken symbols are used for irreducible representations. The main part (second section) contains the character for each of the symmetry operations in columns headed by operations. The top row forms the classes of symmetry. Each class of the symmetry operator is preceded by a number showing the number of operations in that class. The column before the last column displays six symbols: x, y, z, R_x, R_y, R_z. The first three represent the x, y an z-coordinates. R_x, R_y and R_z represent the three rotations about the specified axes. The last column shows the squares and binary products of coordinates according to their transformation properties.

The most symmetric species are placed near the top and the least symmetric species are placed at the bottom of the table. The irreducible representations are of great importance in classifying molecular vibrations, orbitals, quantum states and all other properties of molecules and crystals which are related with the symmetry of the structures. Therefore, the character table are very useful in the solution of many physical problems.

8.22 GREAT ORTHOGONALITY THEOREM

This is the most important theorem of group theory. It deals with the matrix elements which constitutes the irreducible representative. As the name indicates, the theorem shows the orghogonal relationships that exist between the matrix elements of different representations of a group. The theorem is valid for non-equivalent irreducible representations of any group.

Mathematically it may be expressed as

$$\sum_R \Gamma_i (R)_{mn} \Gamma_j (R)_{m'n'} = \frac{h}{\sqrt{l_i l_j}} \delta_{ij}\, \delta_{mm'}\, \delta_{nn'} \qquad (8.28)$$

where Γ_i = ith irreps. of point group of order h having dimension l_i.

Γ_j = jth irreps. of point group of order h having dimension l_j.

$\Gamma_i(R)_{mn}$ is the mnth matrix element corresponding to symmetry element R belonging to ith irrep.

$\Gamma_j(R)_{m'n'}$ complex conjugate of the m'n'th matrix element corresponding to symmetry element R belonging to jth irreps.

$\delta_{ij}, \delta_{mm'}, \delta_{nn'}$ denote the Kronecker delta symbols.

The following three cases arise assuming that matrix elements are real

$$\sum_R \Gamma_i(R)_{mn} \Gamma_j(R)_{mn} = 0 \qquad \text{if } i \neq j$$

$$\sum_R \Gamma_i(R)_{mn} \Gamma_i(R)_{m'n'} = 0 \qquad \text{if } m \neq m' \text{ and/or } n \neq n'$$

$$\sum_R \Gamma_i(R)_{mn} \Gamma_i(R)_{mn} = \frac{h}{I_i} \qquad \text{if } m = m' \text{ and } n = n'$$

Thus, if the vectors differ by being chosen from matrices of different representation, they are orthogonal. If they are chosen from the same representation but from different sets of elements in the matrices of this representation, they are orthogonal. Finally the square of the length of any vector equals $\frac{h}{I_i}$.

Following rules can be derived from orthogonality theorem regarding irreducible representations and their characters.

1. The sum of the squares of the dimensions of the irreducible representations of a group is equal to the order of the group.

$$\Sigma I_i^2 = I_1^2 + I_2^2 + I_3^2 + \ldots = h \qquad (8.29)$$

Since $\chi_i(E)$, the character of the representation of E in the ith irreducible representations, is equal to the order of the representation, we can also write this rule

$$\sum_i [\chi_i(E)^2] = h \qquad (8.30)$$

2. The sum of the squares of the characters in any irreducible representation equals. h, that is,

$$\sum_R [\chi_i(R)^2] = h \qquad (8.31)$$

3. The characters of symmetry operations in two different irreducible representations satisfy the relation

$$\sum_R \chi_i(R)\,\chi_i(R) = 0 \quad i \neq j \tag{8.32}$$

Equations (8.31) and (8.32) can be combined into one equation

$$\sum_R \chi_i(R)\,\chi_j(R) = h\delta_{ij} \tag{8.33}$$

4. In a given representation, the character of all matrices belonging to operations in the same class are identical.

5. The number of irreducible representations of a group is equal to the number of classes of a group.

If we denote the number of elements in the mth class by g_m, the number in the nth class by g_n, and so on, and if there are K classes, equation (8.33) can be written as

$$\sum_{p=1}^{K} \chi_i(R_p)\,\chi_j(R_p)g_p = h\delta_{ij} \tag{8.34}$$

R_p refers any one of the operation in the pth class.

8.23 CONSTRUCTION OF CHARACTER TALES FOR POINT GROUPS

Let us now consider the irreducible representations of C_{2v} point group to see how these rules apply. The group C_{2v} consists of four elements, and each is in a separate class. Hence (rule 5) there are four irreducible representations for this group. But it is also required (rule 1) that sum of the squares of the dimensions of these representations equal h. Thus we are looking for a set of four positive integers, l_1, l_2, l_3 and l_4 which satisfy the relation

$$l_1^2 + l_2^2 + l_3^2 \; l_4^2 = 4$$

Clearly the only solution is

$$l_1 = l_2 = l_3 = l_4 = 1$$

Thus the group C_{2v} has four one-dimensional irreducible representations.

We can actually work out the characters of these four irreducible representations which are in this case the representations themselves because the dimensions are 1 – on the basis of vector properties of the representations and the rules derived above. The suitable vector in 4 – space which has a component of 1 corresponding to E will be

	E	C_2	σ_v	σ_v'
Γ_1	1	1	1	1

for $$\sum_R [\chi_1(R)]^2 = 1^2 + 1^2 + 1^2 + 1^2 = 4$$

this satisfying rule 2. Now all other representations will have to be such that

$$\sum_R [\chi_i(R)]^2 = 4$$

which can only be true if each $\chi_i(R) = \pm 1$. Moreover, in order for each of the other representations to be orthogonal to Γ_1 (rule 3), there will have to be two +1's and two −1's. Thus

$$(1)(-1) + (1)(-1) + (1)(1) + (1)(1) = 0$$

Thus we will have

	E	C_2	σ_v	σ_v'
Γ_1	1	1	1	1
Γ_2	1	−1	−1	1
Γ_3	1	−1	1	−1
Γ_4	1	1	−1	−1

All of these are also orthogonal to one another. For example, taking Γ_2 and Γ_4, we have

$$(1)(1) + (-1)(1) + (-1)(-1) + (1)(-1) = 0$$

and so on. These are then the four irreducible representations of the group C_{2v}.

8.24 DECOMPOSITION OF REDUCIBLE REPRESENTATIONS

During the applications of group theory to chemical problems, we have to deal with characters of reducible representations. The task is to find irreducible representations whose sum is equal to the reducible representation. Following equation is used to decompose reducible representation to irreducible representation.

$$a_i = \frac{1}{h}\left[\sum_R \chi^R \chi_i^R C^R\right] \tag{8.35}$$

where a_i = The number of times the irreducible representations occuring in the reducible representation, Γ_{red}.

h = order of the point group.

R = An operator of the group.

χ^R = Character of operation R in the reducible representation Γ_{red}.

χ_i^R = Character of the operation R in the irreducible representation, Γ_i.

C^R = The number of symmetry operation in the class in which R belong.

To find the values of a_i requires the knowledge of χ_i^R and these values are tabulated in character table.

Let us consider the example of H_2O molecule which belongs to C_{2v} point group. For two H-atoms in water, the matrix representation of the symmetry elements are written as:

$$\begin{array}{ccccc} & E & C_2 & \sigma_v^{xz} & \sigma_v^{yz} \\ 2H & \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} & \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} & \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} & \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \\ \chi & 2 & 0 & 2 & 0 \end{array}$$

Character Table for C_{2v} point group.

C_{2v}	E	C_2	σ_v^{xv}	σ_v^{yz}
A_1	1	1	1	1
A_2	1	1	–1	–1
B_1	1	–1	1	–1
B_2	1	–1	–1	1

$$a(A_1) = \frac{1}{4}[2 \times 1 \times 1 + 0 \times 1 \times 1 + 2 \times 1 \times 1 + 0 \times 1 \times 1] = 1$$

$$a(A_2) = \frac{1}{4}[2 \times 1 \times 1 + 0 \times 1 \times 1 + 2 \times (-1) \times 1 + 0 \times (-1) \times 1] = 1$$

$$a(B_1) = \frac{1}{4}[2 \times 1 \times 1 + 0 \times (-1) \times 1 + 2 \times 1 \times 1 + 0 \times (-1) \times 1] = 1$$

$$a(B_2) = \frac{1}{4}[2 \times 1 \times 1 + 0 \times (-1) \times 1 + 2 \times (-1) \times 1 + 0 \times 1 \times 1] = 1$$

$$\therefore \quad \Gamma_{2H} = \Gamma(A_1) + \Gamma(B_1)$$

QUESTIONS

1. What do you understand the term molecular symmetry? Discuss its significance in chemical sciences.

2. (a) Explain the difference between symmetry elements and symmetry operation with suitable examples.

   (b) The symmetry of an isolated molecule is known as point group symmetry, comment.

3. (a) Discuss the significance of identity as symmetry element.

   (b) What do you mean by proper rotation? Assign the proper rotational axis in the following molecules: OCS; PH_3; benzene; pyridine; SF_4 and SF_6.

   (c) What is principal axis of rotation? Explain it with suitable examples.

4. (a) What is meant by plane of symmetry or mirror plane? Discuss its different forms present with molecular symmetry.

   (b) Assign different types of mirror plane to the following molecules. Ethylene, Br_2; Cyclohexane; BF_3; NH_3, SF_6

5. What is improper rotation? Explain it with suitable examples.

6. Define center of symmetry. Explain its significance with suitable examples.

7. (a) Define a symmetry point group. Explain how a molecule is assigned to a point group?

   (b) What are the rules of group theory? Explain these with suitable examples.

8. (a) Identify various types of symmetry elements in the following point groups. (i) C_{2h} (ii) D_{2d} (iii) C_{4v} (iv) $C_{\infty v}$

   (b) An AX_6 molecule belongs to O_h point group. Find the point groups that will result if the molecule is changed into (i) AX_5Y (ii) Trans-AX_4Y_2 (iii) Cis-AX_4Y_2.

   (c) Find the point groups that result if a center of inversion is added to the symmetry of molecule belonging to (i) C_{4v} (ii) C_2 and (iii) D_6.

9. (a) Compare the elements of symmetry of tetrahedral and octahedral point groups.

   (b) Construct a decision tree diagram to assign a particular point group to a molecule.

   (c) What important symmetry element is absent in PCl_3 molecule that is present in D_{3h} point group?

10. (a) Explain the difference between a point group and space group.

    (b) What are Abelian and non-Abelian groups.

11. (a) Explain the symmetry criteria that allow a molecule to show permanent dipole moment.

(b) Explain why the following molecules possess zero dipole moment (i) CO_2 (ii) Cl_2 (iii) CH_4 (iv) Ethane (Staggered form).

12. (a) Explain the symmetry criteria that allow a molecule to show optical activity or chirality.

(b) Why is the optical activity not shown by the following molecules. (i) Allene (ii) NH_3 (iii) CH_4 (iv) SF_6

13. For each molecule at the left, select the correct point group from the list at right. Some point groups may be represented by more than one molecule.

H_2S

Cl_2

NO

p-dichlorobenzene

SF_5Br

Cyclopropane (ignore Hs)

C_2H_6 (trans)

C_2H_6(cis)

BF_3

C_{2v}

C_{4v}

$C_{\infty v}$

D_{2h}

D_{3h}

D_{3d}

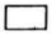
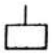
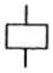
$D_{\infty h}$

14. (a) List the symmetry elements and derive the point group for each of the following molecules: CCl_4, $CHCl_3$; CH_2Cl_2, CH_3Cl, C_2H_5Cl

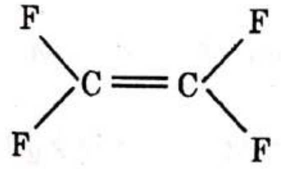
(b) Show the various elements of symmetry in square pyramidal geometry.

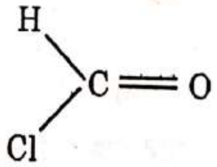
15. Symmetry operations, E, C_2 and $2\sigma_v$ are present in H_2S. Write the multiplication table for this molecule.

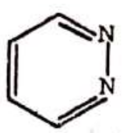
16. Assign the following geometrices to proper point group.

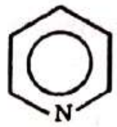
(i) —— (ii) Δ (iii)  (iv)  (v) 

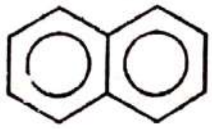
17. Find the symmetry elements and assign the proper symmetry point groups to the following molecules.

(i) 

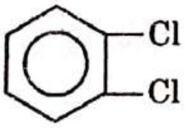
(ii) 

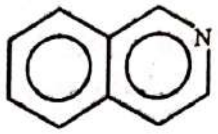
(iii) 

(iv) 

(v) 

(vi) $HC{\equiv}C{-}NO$

(vii) 

(viii) 

(ix) $Cl_3P{=}O$

(x) Tennis ball

(xi) 1,3,5-trichlorobenzene

(xii) Benzophenone

(xiii) SF_5Cl

(xiv) BFClBr

(xv) $(C_5H_5)_2Fe$ (ferroncene)

(xvi) Cl_2O

(xvii) $1F_5$

(xviii) B_2H_6

(xix) PCl_3

(xx) CH_3COOH

(xxi) $[Fe(CN)_6]^{3-}$

(xxii) $Ni(CO)_4$

18. (a) Explain the difference between class and order of a group.

(b) What do you know about similarity transformation. Write down some important properties of conjugate elements.

19. (a) What are matrices? Discuss their significance in group theory.

(b) What is the difference between diagonal and unit matrix?

(c) What is transpose and character of a matrix?

20. (a) Find the inverse of matrix A

$$A = \begin{bmatrix} 5 & 4 \\ 1 & 1 \end{bmatrix}$$

(b) Three matrices A, B and C are given below

$$A = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix},\ B = \begin{bmatrix} 3 & 5 \\ 2 & 5 \end{bmatrix},\ C = \begin{bmatrix} 4 & 4 \\ 4 & 4 \end{bmatrix}$$

Select the matrix which is singular and write it.

21. (a) What do you understand by matrix representation of symmetry operation? Explain it with the example of a unit vector.

(b) Find the matrix representation of symmetry operation in H_2O and boric acid.

(c) Explain symmetry properties of atomic orbitals.

22. (a) What are reducible and irreducible representations. Explain these with suitable examples.

    (b) How would you generate irreducible representations.

    (c) Write irreducible representations of C_{2h} point group.

23. (a) Write some important features of irreducible representations.

    (b) What is character table? Discuss its significance in group theory.

    (c) Write character table for the following point groups:

    (i) C_{2v}, (ii) C_{2h}, (iii) T_d and (iv) C_{3v}.

24. (a) What is great orthogonality theorem? Discuss its significance in group theory.

    (b) Explain decomposition of reducible representation.

25. Justify/comment on the following statements.

    (i) Symmetry element and symmetry operations are same thing.

    (ii) Symmetry is a widely distributed property in nature.

    (iii) BF_3 has C_3 axis of rotation.

    (iv) Cl_2O belongs to C_{2V} point group.

    (v) Td and On are special point groups.

    (vi) $CHCl_3$ belongs to tetrahedral group.

    (vii) Rose flower has symmetry.

    (viii) Apple belongs to $C_{\infty V}$ point group.

    (ix) Square planner geometry has C_{4h} point group.

REFERENCES

1. Cotton, F. A. 1990. Chemical Applications of Group Theory, Wiley, New Jersey.
2. Carter. R. L. 1998. Molecular symmetry and Group Theory, John Wiley and Sons, Inc. New York.
3. Peter, A. and D. P. Paula, 2002. Atkin's Physical Chemistry, 7th Edition, Oxford University press, London.
4. Silbey, R. J. Alberty, R. A. and M. G. Bawendi. 2005. Physical Chemistry, Wiley, India.
5. K.V. Remann 1990. Group Theory and its Applications to Chemistry. Data Mc Graw Hil Publishing (O), New Delhi.
6. Mohammad, A. 1984, Application of Symmetry and Group Theory in Chemistry VGC, Islamabad.
7. Barrow, G.M. 1995. Introduction to Molecular Spectroscopy, McGraw-Hill, New York.

Chapter 9

ELECTROCHEMISTRY

9.1 INTRODUCTION

Electrochemistry is a branch of Physical Chemistry which deals with the study of all physical and chemical processes which are brought about by electrical energy and the processes which proceed with the generation of electrical energy. It concerns itself with the interrelation of electrical energy (electricity) and chemical phenomena i.e. the conversion of electrical energy into chemical energy and vice versa. Simply one can say that electrochemistry deals with the relationship between the electrical energy and chemical changes.

Much of the Chemistry involves species that have charge. Electrons, cations and anions all are charged particles that interact chemically. Often electrons move from one chemical species to another to form something new. These movements can be spontaneous, or they can be forced. They can involve systems as simple as hydrogen and oxygen atoms, or as complex as million-peptide protein chain. The presence of discrete charges on chemical species introduces a new aspect that we must consider, the fact that like charges repel and opposite charges attract. In considering how charged particles interact, we have to understand the work involved in moving charged particles together and apart, and the energy required to perform that work. Energy, work-these are concepts of thermodynamics. Therefore, our understanding of chemistry of electrically charged particles, *electrochemistry*, is based on thermodynamics.

Electrochemistry is concerned with the appearance and disappearance of electrical energy in the surroundings when the chemical reactions occur in a system, it is necessary that the system must be electrically conducting. Such a communication between the system and surrounding can be achieved by using either a metallic or an electrolyte conductor. It is, in fact, the study of latter, which is generally assumed to fall under the purview of electrochemistry. For the fact that electrolytic solutions need a metallic conductor for developing an electrical contact, the electrochemistry, to be more specific involves the study, or processes at the metal-electrolyte and electrolyte-electrolyte interfaces.

Few people realize the applications of electrochemistry in modern life. All batteries and fuel cells can be understood in terms of electrochemistry. Batteries, which produce, electrical energy by means of chemical reactions, are used to power toys, flash light, electronic calculators, pacemakers, that maintain the rhythm of heart, radios, tape recorders and even some automobiles (hybrid cars). Any oxidation-reduction process can be considered in electrochemical terms. In the laboratory electrical measurements enable us to monitor chemical reactions of all sorts, even there is systems as tiny as living cells. In industry many important chemicals-including liquid bleach (sodium hypochlorite) and lye (sodium hydroxide which is used to manufacture soap) are manufactured by electrochemical reactions. In fact, if its were not for electrochemical reactions, the important structural metals (aluminium and magnesium) would be only laboratory curiosities. Corrosion of metals, non-metals and ceramics is electrochemistry. Besides the practical applications fundamental information about the chemical reactions is available from the electrical measurements, for example, free energy changes, equilibrium constants etc. Many of the virtually important biochemical reactions involve the transfer of charge, which is electrochemistry.

Electromechanical processes non-a-days have found wide applicability. The electrolytic and electrosynthetic methods are frequently employed for the preparation of chemical products. Electrochemical methods of analysis, e.g., electrolysis, conductometry, potetniometry, polarography, voltametry etc., have been greatly developed in the recent years.

9.2 CONDUCTORS AND INSULATORS

We know that electrical energy or electricity is a stream of electrons. The substances which allow the passage of electricity or electric current through them are called *conductors*. It may, however, be pointed out that not all the conductors conduct electricity to the same current. Depending upon the ease with which they allow the passage of electricity they are named as *good conductors* or *bad conductors*. Although it is not possible to sharply distinguish between the good or bad conductors, but a rough division is possible on the basis of relative ease with which the conductors allow the passage of electric current. The substances which do not conduct electric current are called *insulators* or *non-conductors*, e.g. wood, rubber etc.

Conductors, in general, can be classified into three categories, viz. gaseous metallic and electrolytic.

(i) The gases conduct electric current under high potential differences at low pressure, or when exposed to certain radiation.

(ii) In the metallic or electronic conductors, the charge carriers are the electrons, the atomic nuclei remaining stationary, and the passage of electric current is not accompanied by any movement of matter. Such a mode of conduction of electric current is called *metallic* or *electronic conduction*. It is exhibited by pure metals, alloys, carbon and certain solid salts and oxides. Metallic conductors are the best conductors of electric current. This mode of conduction decreases with rise in temperature.

(iii) The *electrolytic conductors* (also known as ionic conductors) transport electric current through the movement of charged particles of atomic or molecular dimensions called *ions*. Since ions are heavy, the electrolytic conductor are less conducting as compared to metallic conductors. The ionic conduction increases with rise in temperature. Solutions of salts, acids and bases in water or some other solvents are examples of ionic conductors.

The above classification of conductors is a relative one. Certain solids like β-Ag_2S, ZnO, CuO etc. exhibit mixed conductivity. A transition from electrolytic to mixed conductivity is also observed in some salts, e.g. Cu_2Cl_2 when they are heated. A similarly transition to mixed conductivity is observed in solutions of the alkali and alkaline earth metals in liquid ammonia at higher salt concentrations. Conduction of current through metallic and ionic conductors may be briefly distinguished as given below.

Metallic Conduction	Ionic Conduction
(i) It is by virtue of flow of electrons in the conductor.	(i) It is by virtue of the movement of ions in the solution or a fused electrolytes.
(ii) It involves no change in the chemical properties of the conductor.	(ii) It involves chemical reactions which take place at electrodes e.g. oxidation-reduction.
(iii) It does not involve the transfer of matter.	(iii) It involves the transfer of matter in the form of ions.
(iv) It decreases with rise in temperature offered to the moving electrons by the oscillating atoms or ions composing the conductors.	(iv) It increases with rise in temperature due to increase in the mobility of ions and increase in the degree of ionization of electrolytes.

9.3 OHM'S LAW AND ELECTRICAL UNITS

An electrolytic solution contains free ions in addition to other kinetically identifiable species. When an electrical potential is applied across the solution, the macroscopic observations arc; the flow of the current through the solution and the chemical changes generally resulting in the liberation or dissolation of the electrode material at the points where the current enters or leaves the solution. This phenomenon of decomposition of solution by electric current is termed *electrolysis*. The relationship between the applied potential and the current flowing is given by Ohm's law.

According to Ohm's law the strength of an electric current (I) flowing through a conductor is directly proportional to the potential difference applied (V) across the conductor and inversely proportional to the resistance (R) offered by the conductor to the current, i.e.,

$$I = \frac{V}{R} \qquad (9.1)$$

By making appropriate choice of units, the constant of proportionality is made unity. According to International System, the units of current, resistance and potential are ampere, ohm and volt respectively.

The international ampere is defined as the invariable current of such strength that on passing through an aqueous silver nitrate solution will deposit 0.001118 g of silver in one second.

The international ohm is defined as the resistance at 0°C of a column of uniform cross section, 106.3 cm long and containing 14.4521 of g mercury.

The international volt is defined as the potential difference required to send a current of one ampere through a resistance of one ohm.

The quantity of electricity is measured in *international coulomb*. It is the quantity of electricity passing through a conductor when a current of one ampere flows in one second. Hence the quantity of electricity is given by the relation.

$$Q = I \times t \tag{9.2}$$

Another unit to measure the quantity of electricity is the *Faraday* (F). It is equal to 96,500 coulombs. The main significance of F is that it is the amount of charge that produces one equivalent of chemical change.

The electrical work (W) performed when a current of strength I passes for t second through a resistance across which the potential difference is V, is given by

$$W = VIt = VQ \tag{9.3}$$

where W is expressed in joules. The Joule is the electrical unit of energy and is defined as the amount of work performed by a current of one ampere flowing for one second under a potential difference of one volt.

$$1J = 1 \times 10^7 \text{ ergs} = 0.2390 \text{ cal}$$

Finally, the rate at which work is being done by an electric current is expressed in watt. A *watt* is worked performed at the rate of 1 Joule per second, and is a unit of electrical power.

9.4 ELECTROLYTIC CONDUCTANCE

Electrolytes or ionic conductors are good conductors of electricity. The electrical conductance of an electrolyte is due to the ions it contains. The greater the concentration of the ions, the higher will be the conductance. The interesting feature of electrolytic solutions is not that they resist the flow of electricity, but that they allow it to flow. Consequently, the important value in electrochemistry is conducting power. The conductance (L) of a system is reciprocal of its resistance (R). Thus conductance is defined as

$$L = \frac{1}{R} \tag{9.4}$$

The SI unit of conductance is Siemen (symbol S). Since resistance (R) is measured in ohms (symbol Ω, omega), its reciprocal, the conductance is defined with the units of reciprocal ohm, ohm^{-1} or mho and denoted as Ω^{-1} (omega inverse). Following the SI system of units, we shall use S to define the conductance.

To compare the conductivity of different solutions, the size of the electrodes and the distance between the electrodes must be standardized. It has been found that the resistance offered by a solution is directly proportional to the distance between the electrode and inversely proportional to the area of the cross section of solution between the electrodes

$$R \propto \frac{l}{A}$$

$$R = \rho \frac{l}{A} \tag{9.5}$$

where l is the difference between the electrodes, A is the area of cross section and ρ(rho) is the constant of proportionality known as the *specific resistance* or *resistivity*. If in the above equation l = 1m, A = 1m^2, then R = ρ. Hence the specific resistance is the resistance of a conductor of unit length and of a unit area of cross section. In other words, specific resistance is the resistance of a meter cube of the material. The SI units of the specific resistance is ohm.m or Ω.m.

The *specific conductance* or *conductivity* of any conductor is defined as the reciprocal of the specific resistance. It is represented by Ls.

Since $\quad Ls = \frac{1}{\rho}$

Equation (9.5) becomes

$$\rho = R \cdot \frac{A}{l}$$

$$\frac{1}{\rho} = \frac{1}{R} \cdot \frac{l}{A}$$

Hence $\quad Ls = \frac{1}{R} \cdot \frac{l}{A} \qquad \left(\therefore \ L = \frac{1}{R} \right)$

$$Ls = L \cdot \frac{l}{A} \tag{9.6}$$

Now if l = 1m, and A = 1m^2, then

$$Ls = L \tag{9.7}$$

Hence the specific conductance is the conductance of a material of unit length and unit area of cross section.

Alternatively, specific conductance is the conductance of a one meter cube of the material. For electrolytic solutions, it is the conductance of a meter cube of the solution. Since the specific resistance is measured in ohm × m, the units of the specific conductance will be ohm^{-1} · m^{-1} or mho m^{-1} or S m^{-1}.

Conductance (L) and specific conductance (Ls) are additive properties. If a number of electrolytes are present together in a dilute solution, the total conductivity is equal to the sum of Ls values of individual electrolytes.

$$Ls = \sum_i Ls_i + Ls_{H_2O}$$

Likewise $\quad L = \sum_i L_i + L_{H_2O}$

where $\sum_i Ls_i$ denotes the sum of the conductivities of all the electrolytes present in the solution and Ls_{H_2O} is the conductivity of water. By repeated distillation of water with small amounts of $KMnO_4$ added to it (to oxidize organic impurities) specific conductance of water (Ls_{H_2O}) can be reduced to minimum. Water prepared in this manner is called conductivity water ($LsH_2O = 1 \times 10^{-8}$ S m^{-1}). Conductivity water is used for preparing solutions of electrolytes for conductivity measurements.

9.5 EQUIVALENT AND MOLAR CONDUCTANCE

At any fixed temperature, the conductivity of a solution depends partly on the number of charges per unit volume, which for different solutions may contain different amounts of electrolytic charges. Since the point of interest is to compare the current carrying ability of a given number of electrolytic charges at different concentrations, it is not much rewarding to consider the conductivity/specific conductance as a fundamental quantity. In order to compare the conductance of an electrolyte with another electrolyte, the fundamental weight of an electrolyte must be dissolved in the same volume of the solution. This weight is either the equivalent weight or the molecular weight.

The *equivalent conductance* of an electrolyte is defined as the conductance of a volume of the solution containing one gram equivalent of dissolved substance when placed between two parallel electrodes 1m apart, and large enough to contain between them all of the solution. It is represented by Λ (lambda) and never determined directly, but is calculated from the specific conductance. It represents the conductivity power of all the ions produced by dissolving one gram equivalent of the electrolyte at a given dilution and temperature.

$$\Lambda = Ls \times V \tag{9.8}$$

If C represents the concentration of a solution in gram equivalent per litre, then the volume containing one equivalent of the electrolyte is $\frac{10^{-3}}{C}$ m^3. If Ls represents the specific conductance S m^{-1}, then the equivalent conductance is given as

$$\Lambda = \frac{Ls \cdot 10^{-3}}{C} \tag{9.9}$$

The units of equivalent conductance are S m^2 eq^{-1}, but in common use the last term is generally dropped out. The SI unit is S m^2.

Another quantity which is quite often used is the *molar conductance* (μ). it is defined as the conductance due to ions produced by one mole of the electrolyte at a given dilution and temperature. It may be defined as the conductance of a volume of a solution containing one mole of the electrolyte when placed between two parallel electrodes 1m apart and large enough to contain between them the whole of the solution. It is equal to the product of specific conductance (Ls) and volume of the solution containing one mole of the electrolyte.

$$\mu = Ls \times V$$

If C represents the concentration in mole per litre, then

$$\mu = \frac{Ls \cdot 10^{-3}}{C} \text{ S m}^2 \text{ mol}^{-1} \qquad (9.10)$$

$\wedge$ is related to the μ through the relation

$$\wedge = \frac{\mu}{\text{Total no. of equvialents of cationic (or anionic)charges per mole of salt}} \qquad (9.11)$$

or $$\wedge = \frac{\mu}{Z} \qquad (9.12)$$

where Z = total positive charge carried by cations or total negative charge carried by anions furnished by a molecule of an electrolyte on dissociation. For example,

$NaCl \longrightarrow Na^+ + Cl^-$ (Z = 1)

$CaCl_2 \longrightarrow Ca^{2+} + 2Cl^{-1}$ (Z = 2)

$Al_2(SO_4)_3 \longrightarrow 2Al^{3+} + 3SO_4^{2-}$ (Z = 6)

9.6 MEASUREMENT OF CONDUCTANCE

The conductance of a solution of an electrolyte can be determined by measuring the resistance offered by the solution contained within the two electrodes of a conductivity cell. By knowing the resistance, one can determine the conductance just by reciprocating the resistance. The measurement of the resistance is most frequently carried out with some form of Wheatstone bridge circuit, the principle of which may be explained with the aid of Fig.9.1. Four resistance R_1, R_2, R_3 and R_4 are connected in such a way so as to form a loop/mesh ABCDA. A battery of emf 'E' is connected between point B and D and a galvanometer 'G' is connected between A and C. This circuit is known as Wheatstone bridge circuit. The bridge is said to be balanced if no current from battery E flows through the galvanometer G. When no current flows through the galvanometer, it means that the potential difference from the one terminal of the galvanometer to the other terminal of the galvanometer is the same. This is known as balancing condition of the bridge. Galvanometer is a device which detects small amount of electric current.

The solution whose conductance is to be found out in terms of resistance, is placed in a special type of cell, called conductivity cell. It is placed in one arm of the bridge and a variable standard resistance (Rs), e.g. a resistance box in the other arm. AC is a uniform slide wire across which moves a contact point D. The resistance Rs is such adjusted that when the contact point D is moved along AC, the galvanometer shows no deflection, i.e. the null point is obtained. One can also use some other

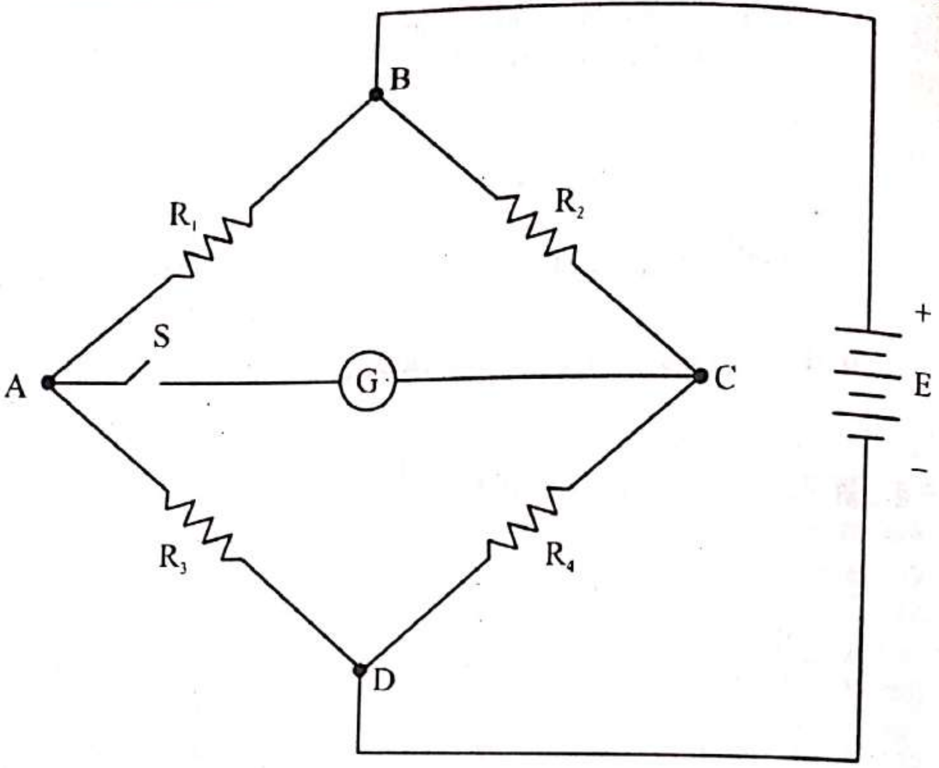


Fig. 9.1 Wheatsonte bridge circuit for resistance measurement

detecting devices like earphone, which gives minimum sound at the null point. When this state of balanced is achieved, the two terminals of the detector are at the same potential. The potential difference across the different parts of the bride must be such that

$$E_X = E_S \tag{9.13}$$

and $$E_a = E_b \tag{9.14}$$

According to Ohm's law ,the difference of potential E, is equal to the current (I) and the resistance (R)

$$E_X = R_X \times I_X \qquad E_S = R_s I_s$$

$$E_a = R_a I_a \quad \text{and} \quad E_b = R_b I_b$$

According to Equ. (9.13) and (9.14)

$$R_X \times I_X = R_s I_s \tag{9.15}$$

$$R_a I_a = R_b I_b \tag{9.16}$$

Dividing Eq. (9.15) by Eq. (9.16), we get

$$\frac{R_X I_X}{R_a I_a} = \frac{R_s I_s}{R_b I_b} \tag{9.17}$$

Further $I_X = I_a$ and $I_s = I_b$, since the current flowing through two resistances in series must be same in each resistance.

Under the balanced conditions, when no current flows through the detector, then Eq. (9.17) reduces to

$$\frac{R_X}{R_a} = \frac{R_s}{R_b}$$

$$R_X \text{ (unknown)} = \frac{R_a}{R_b} \times R_s \qquad (9.18)$$

The resistance R_a and R_b are proportional to the length of the wire AD and CD respectively. Thus, we have

$$R_X = \frac{\text{Length AD}}{\text{Length CD}} \times R_s \qquad (9.19)$$

Since R_s, length AD and CD are known, the resistance R_X of the solution can be calculated, from which one can determine the conductance, specific conductance and equivalent/molar conductance. As the conductance is affected by the temperature, the conductivity cell is always placed in the thermostat which is maintained at constant temperature. (Fig. 9.2)

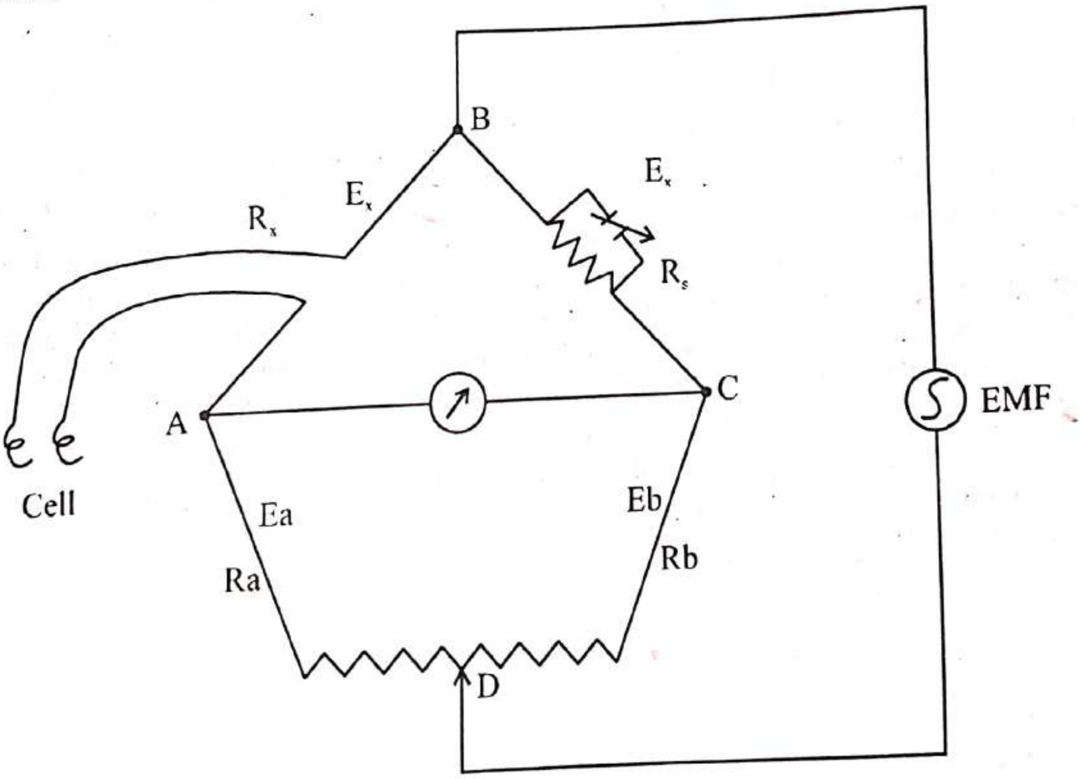


Fig. 9.2 A.C. Wheatstone bridge for conductance measurement

Although the principle of the Wheatstone bridge as given above remains the same several modifications in technique are necessary before resistance of an electrolytic solution can be measured by this method. Direct method cannot be used, as this would cease electrolysis and concentration changes at the electrodes. The gas if liberated increases the resistance at the electrodes. These gases also set up a counter emf of polarization which opposes the passage of the current. To avoid these, an alternatively current is employed, usually a frequency of 500 — 2000 Hz is supplied by either a vibrating tuning fork or a vacuum-tube oscillator. In AC current, the direction of the current is reversed about a thousand times per second with the result that the polarization produced by each pulse of the current is neutralized by the next pulse.

The conductivity cells are constructed of glass with electrodes of either platinum or gold. To overcome imperfections in the current and other effects, so as to decrease the effects of polarization of electrodes, the electrodes are coated with a layer of finely divided platinum black. This is done by electrolysis of 3% solution of chloroplatinic acid containing traces of lead acetate. If the finely divided platinum serves either as a catalyst for decomposition or oxidation of the solution or as an adsorbents for adsorption of ions, the grey platinum surface electrodes may be employed instead. The latter can be obtained by heating the platinized electrode to red heat.

9.7 CELL CONSTANT

The specific conductance of an electrolytic conductor is defined as

$$L_s = \frac{1}{R} \cdot \frac{l}{A}$$

$$L_s = L \cdot \frac{l}{A} \qquad (9.6)$$

where l may be taken as the distance between the electrodes in conductivity cell and A is the area of cross section of each electrode. Before L_S can be calculated from the measured resistance, the ratio (l/A) for a particular cell used, is required. For any given cell, the ratio has a fixed value, called the *cell constant* K, which can be obtained without knowing the actual values of l and A. It can also be obtained by direct measurements, but this is rarely done, since it is possible to evaluate it by means of a solution of known specific conductance. Potassium chloride is the accepted standard for which accurately determined values of L_S at different concentrations and temperatures in aqueous solution are available. A given solution of KCl of specific conductance is placed in the cell and its resistance is measured. The cell constant is equal to

$$K = L_S \times R$$

$$K = \frac{\text{Specific conductance}}{\text{Observed conductance}} \qquad (9.20)$$

Hence, cell constant is a factor which when multiplied by the observed conductance of a solution, gives its specific conductance. KCl is available in pure state. It is 1 : 1 electrolyte and ionic mobilities of K^+ and Cl^- ions are comparable. The ionic radii of both ions are equal. Its values of specific conductance are available in the literature at different concentrations and temperatures. The dimensions of cell constants are

$$K = \frac{l}{A} = \frac{m}{m^2} = \frac{1}{m} = m^{-1}$$

Table 9.1 shows the specific conductance of 0.01, 0.1 and 1.0 N solutions of KCl at different temperatures.

Table 9.1 Specific Conductance of KCl solutions

Concentration eqiv. dm^{-3}	LS ($S\ m^{-1}$)		
	273 K	291 K	298 K
1.0	6.5170	9.7840	11.1900
0.1	0.7140	1.1166	1.2890
0.01	0.0774	0.1221	0.1413

Example 9.1

A conductivity cell was filled with 0.01 M KCl which was known to have a specific conductivity of 0.1413 S m^{-1} at 298 K. Its measured resistance at 298 K was 94.3 ohms. When the cell was filled with 0.02 M $AgNO_3$, its resistance was 50.3 ohms Calculate (i) the cell constant, (ii) the specific conductance of $AgNO_3$ solution.

Solution

Here $Ls = 0.1413\ S\ m^{-1}$

$R = 94.3$ ohms

(i) Using the relation

$$L_s = \frac{1}{R} \cdot \left(\frac{l}{A}\right)$$

$$\left(\frac{l}{A}\right) = \text{cell constant} = L_s \times R$$

$$= (0.1413)\ (94.3)$$

$$= 13.32\ m^{-1}$$

(ii) Now $R = 50.3$ ohms

$$\frac{l}{A} = 13.32\ m^{-1}$$

$$L_s = \frac{1}{R} \cdot \left(\frac{l}{A}\right)$$

$$= \frac{13.32}{50.3}$$

$$= 2.648 \times 10^{-1}\ S\ m^{-1}$$

Example 9.2

The resistance of a conductivity cell was 720 ohms when filled with 0.1 N KCl solution (specific conductance = 0.14807 S m^{-1}) and 6920 ohms when filled with 0.01 N acetic acid solution. Calculate cell constant and equivalent conductance of the acid solution.

Solution

The cell constant is given as

$$\left(\frac{l}{A}\right) = L_s \cdot R$$
$$= (0.14807)\,(702)$$
$$= 103.94\ m^{-1}$$

The specific conductance of acetic acid is given by

$$L_s = \frac{1}{R} \cdot \left(\frac{l}{A}\right)$$
$$= \frac{103.94}{6920}$$
$$= 1.50 \times 10^{-2}\ S\ m^{-1}$$

Now $C = 0.01\ N = 0.01\ mol\ dm^{-3}$

Therefore,

$$\wedge = \frac{Ls}{C} \times 10^{-3}$$
$$= \frac{1.50 \times 10^{-2}}{0.01} \times 10^{-3}$$
$$= 1.5 \times 10^{-3}\ S\ m^2\ eqiv^{-1}$$

9.8 VARIATION OF CONDUCTANCE WITH CONCENTRATION

We know that the specific conductance of a solution increases with increasing concentration. For strong electrolytes, the increase in specific conductance with increase of concentration is sharp. However, for weak electrolytes, the increase in specific conductance is more gradual. In both cases, the increase in conductance with concentration is due to an increase in the number of ions per unit volume of the solution. For strong electrolytes, which are completely ionized, the increase in specific conductance is almost proportional to the concentration. In weak electrolytes, however, the increase in specific conductance is not large due to low ionization of the electrolytes, and consequently the specific conductance does not go up so rapidly as in the case of strong electrolytes.

Table 9.2 shows the variation of equivalent conductance of a number of electrolytes at various concentration at 298 K. It is observed that in contrast to the specific conductance, the equivalent conductance Λ invariably increases with decreasing concentration for both weak and strong electrolytes.

Table 9.2 Equivalent Conductance of Electrolytes in Aqueous Solutions at 298 K ($10^4 \times$ S m^2 equiv.$^{-1}$)

Equivalent Per liter	KCl	NaCl	HCl	$AgNO_3$	CH_3COH	CH_3COONa
1.0	111.9	89.9	332.8	–	–	49.1
0.1	129.0	106.7	391.3	109.1	5.2	72.8
0.05	133.4	111.1	399.1	115.7	7.4	76.9
0.01	141.3	118.5	412.0	124.8	16.3	83.8
0.005	143.5	120.6	415.8	127.2	22.9	85.7
0.001	146.9	123.7	421.4	130.5	49.2	88.5
0.0005	147.8	124.5	422.7	131.4	67.7	89.2

The above results are depicted in Fig.9.3 in which the equivalent conductance, Λ, of electrolytes at a constant temperature is plotted against $\sqrt{C}$. It may be seen from the figure that two different types of behaviours are exhibited. The electrolytes which show a linear plot (almost straight lines) are classed as strong electrolytes. e.g. salts like NaCl, KCl or acids such a H_2SO_4, HCl etc. The electrolytes which seem to approach the dilute solution limits almost tangentially are classed as weak electrolytes, e.g. ammonia, acetic acid etc. It is however, impossible to draw a sharp line of demarcation between the two categories as many substance are known to exhibit intermediate behavior, e.g., $NiSO_4$. Such electrolytes are sometimes called moderately strong electrolytes.

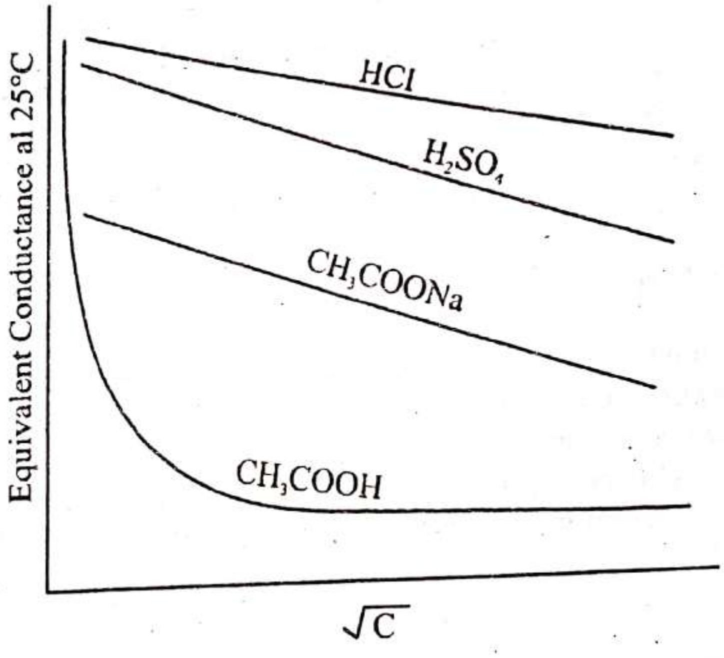


Fig.9.3 Equivalent conductance of strong and weak electrolytes

The conductance of a solution depends on the number of ions and the speed with which the ions move in solution. In case of strong electrolytes, the number of ions is the same at all dilutions (since strong electrolytes are completely ionized) and the variation of equivalent conductance with dilution is therefore due to the change in the speed of the ions with dilution. In a concentrated solution of such electrolytes, the interionic attractions among the oppositely charged ions would be quite appreciable. The ions may also form some ion-pairs of the type A^+B^- which would not contribute to the conductance. These interionic forces considerably lower the speed of ions and hence the conductivity of the solution. As the dilution is increased the interionic attractions decrease with the result that the ions will move more freely and independently of their co-ions and thus increasing the equivalent conductance with dilution.

In case of weak electrolytes, the increase in equivalent conductance with dilution is mainly due to (a) an increase in the number of ions in the solution (degree of ionization increases with dilution), and (b) smaller inter-ionic attractions at higher dilutions.

For weak electrolytes, the increase in the number of ions has been explained on the basis of Arrhenius theory of electrolytic dissociation whereas the strong electrolytes has been explained on the basis of Debye-Huckel-Onsager theory. In brief, the increase in the number of ions in case of weak electrolytes is due to the increase in the degree of ionization of the electrolyte on dilution, whereas in the case of strong electrolytes, this increase is due to the weakening of the ion-ion interactions on dilution.

9.9 EFFECT OF TEMPERATURE ON THE CONDUCTANCE

The conductance of all electrolytes increases with temperature. The variation of equivalent conductance at infinite dilution ($\wedge_0$) with temperature can be represented by the equation

$$\wedge_{t^\circ} = \wedge_{25^\circ} [1 + \beta(t - 25)] \tag{9.21}$$

where $\wedge_{t^\circ}$ is the limiting equivalent conductance at t°C, $\wedge_{25^\circ}$ that at 25°C, and β a constant for each electrolyte. The increase in the equivalent conductance may be explained in terms of increase in the effective degree of dissociation at higher temperature or can be rationalized in terms of lowering of restricting potential for migration with rise in temperature (or change in the mobility of the ions). Equivalent conductance at infinite dilution at ordinary temperatures increases by about 2% per degree.

For salts β is about 0.019 to 0.021, so that the equivalent conductance at infinite dilution at ordinary temperatures increases by about 1.9 to 2.2% per degree. Acids and bases have smaller temperature coefficients (β values) they are approximately 0.018 respectively. It is an evident that an equation similar to (9.21) must hold for individual ion conductances and for nearly all ions, except H^+ and OH^-. For H^+ the value of β is 0.0142 and for OH^- it is 0.016. As a rough generalization, it may be said that the higher the ionic conductance, the smaller the temperature coefficient.

The above results apply particularly to infinite dilution, but similar conclusions hold for strong electrolytes at appreciable concentration. Weak electrolytes however, show some abnormalities; the conductance of such solutions is mainly dependent on the degree of ionization. This usually decreases with rise in temperature, the conductance, may increase to maximum and then decrease as the temperature is raised.

The conductance of a solution varies slightly with pressure, the effect being mainly due to the change in the viscosity of the medium, and consequently alternation in the speed, and hence the conductance, of ions. The viscosity of a dilute solution is generally decreased by an increases of pressure; this is accompanied by an increase of the equivalent conductance, provided the pressure is not too high. This effect is more marked with a weak than with a strong electrolyte; increase of pressure favours the ionization in case of weak electrolyte.

9.10 EFFECT OF DIELECTRIC CONSTANT OF THE SOLVENT ON CONDUCTANCE

The conductance behaviour observed in non-aqueous solvents depends much on the dielectric constant of the medium. The dielectric constant of water is high, 78.6 at 25°C, whereas that of most other solvents is considerably lower. The dielectric constants at 25°C for methanol, ethanol and dioxane arc, 31.5, 24.3 and 2.2 respectively. As the dielectric constant of the solvent is lowered, the conductance of the electrolyte in the medium also decreases. Beyond this conductance drop, the conductance behaviour of these substances is not very different in nonaqueous solvents from that in water, provided the dielectric constant is above 25.

For examples, the halides and nitrates of alkaline metals, the thiocyanates of alkali and alkaline earth metals, and the tetraalkyl ammonium salts are strong electrolytes in methyl and ethyl alcohols and behave pretty much as do strong electrolytes in water. In solvents of dielectric constant less than 25, the dependence of equivalent on concentration becomes complex. In these solvents ions exhibit a tendency to associate into complexes such a $A^+ B^-$, $A^+B^-A^+$ and $A^-A^+B^-$ which decreases the number of ions available to carry current, and hence the conductance.

9.11 EFFECT OF VISCOSITY ON CONDUCTANCE

It has been observed that the movement of an ion is not influenced by other ions in an infinitely dilute solution, so the movement may be considered to be identical with the movement of a spherical particle in a medium of viscosity η. That is to say that Stokes's law may be applied to the movement of an ion. It follows that the product of the speed of the ion and the viscosity of the medium should be constant. The equivalent conductance of an ion at infinite dilution depends only on its speed, and so the product of ion conductance and viscosity should be independent of the nature of the solvent. This relationship known as *Walden's* rule was put forward by P. Walden (1906) in the form

$$\Lambda_0\eta_0 = \text{constant} \tag{9.22}$$

for a given electrolyte, when η_0 is the viscosity of the solvent in which the equivalent conductance at infinite dilution is Λ_0. The Walden's rule may be stated in words as: "The product of limiting equivalent conductance of a given solute and viscosity of the pure solvent is constant."

The constant in Eq. (9.22) is independent of temperature and nature of the solvents and the value of $(C_2H_5)_4$ NI in more than 30 solvents at 0°C is 0.70, i.e.,

$$\Lambda_0\eta_0 = 0.70$$

The above rule of Walden does not apply to water and glycol as solvents. For water $\Lambda_0\eta_0 = 1$ and the value of constant was observed to vary with the nature of solute. A particular ion does not have the same effective radius in different solvents. It is probable that the ions are solvated in the solution. Since the extent of solvation as well as the size of solvating molecules, varies with the nature of the solvent, the effective radius will not be constant. The ions have different effective radii in different solvents due to difference in the extent of solvation. As the solvation effects are quite prominent for smaller ions (particular small cations), the deviation from the Walden's rule would be quite severe for smaller cations. Larger cations do not undergo solvation to an appreciable extent, and hence the Walden's product for such ions remains constant even in different types of solvents.

9.12 ARRHENIUS THEORY OF ELECTROLYTIC DISSOCIATION

In order to explain the behavior of solutions of electrolytes, Arrhenius (1887) put forward the theory of electrolytic dissociation in aqueous solutions. The main points of this theory in this modern form may be summed up as follows:

(i) The electrolytes in solution are dissociated into electrically charged particles called ions. The positively charged particles are called cations and the negatively charged particles are known as anions. A dynamic equilibrium exists in the solution between the undissociated molecules and the ions which dissociate from the electrolytes, that is

$$MA \rightleftharpoons M^+ + A^-$$

(ii) The ions are free to move independently under the influence of an applied electric field. Cations move towards the negative electrode or cathode and the anions move towards the positive electrodes or anode.

(iii) The number of positively charged cations and negatively charged anions may be different. However, the total charge carried by cations is equal to the total charge carried by anions. The net result is that the solution as a whole is electrically neutral in spite of the presence of charged particles.

(iv) The extent of dissociation is different for different electrolytes and depends on the concentration of electrolyte, temperature and nature of electrolyte.

The amount of electrolyte which dissociates into ions varies with its concentration. It may then be anticipated from the law of chemical equilibrium that the extent of dissociation increases with the decrease in concentration and attains a limiting value at very high dilution. At extreme dilutions, all the electrolytes are completely dissociated into ions. The fraction of the total number of molecules dissociated, is called the degree of dissociation (α). Thus

$$\alpha = \frac{\text{Number of molecules dissociated}}{\text{Total numbr of molecules}}$$

Calculation of the degree of dissociation for various electrolytes in aqueous solutions show that practically all salts, and strong acids and bass are highly ionized in water. These are known as strong electrolytes. Aqueous solutions of these electrolytes are therefore good conductors of electricity. On the other hand, there are many substances whose aqueous solutions are poor conductor of electricity. These include many organic acids and bases (such as acetic acid, benzoic acid, methyl amine, aniline etc.), inorganic acids and bases (such as carbonic acid, hydrocyanic acid, ammonium hydroxide etc.). These are called weak electrolytes. This division into strong and weak electrolytes is a qualitative one. There are some electrolytes such as $BaCl_2$ etc. which exhibit an intermediate behaviour.

Limitations of the Arrhenius Theory

Arrhenius theory is satisfactory for weak electrolytes. However, when applied to strong electrolytes many anomalies have been observed which seriously question the validity of some of the postulates of theory. Some of the important discrepancies are:

(i) The degree of dissociation obtained from conductivity measurement and from colligative properties are in good agreement for weak electrolytes. But for the strong electrolyte the agreement is very poor.

(ii) The Ostwald's dilution law is obeyed by weak electrolytes but not all by strong electrolytes.

(iii) Arrhenius theory assumes the existence of ions but does not take into account the electrostatic attraction between ions. The effect of interionic attractions is quite small in solutions of weak electrolytes, but in case of strong electrolytes, this effect is quite pronounced.

These points conclude that Arrhenius theory is essentially valid for weak electrolytes but does not describe the behavior of strong electrolytes.

9.13 THE OSTWALD'S DILUTION LAW

Arrhenius theory of electrolytic dissociation assumes a dynamic equilibrium between ions and unionized molecules. The law of mass action can also be applied to equilibrium involving ions in the same manner as was done in chemical equilibrium. The application of the law of mass action to the weak electrolytes was first attempted by Ostwald (1888) and the equation deduced by him is known as Ostwald's dilution law.

Consider a binary electrolyte AB which dissociates into charged ions A^+ and B^- according to the equation

$$AB \rightleftharpoons A^+ + B^-$$

Applying the law of mass action, we get

$$K_a = \frac{[A^+]\,[B^-]}{[AB]} \qquad (9.23)$$

Let α be the degree of dissociation (or ionization) and C the total concentration of the electrolyte in moles per dm^{-3}. At equilibrium, the concentration of various species would be

$$[A^+] = C\alpha$$

$$[B^-] = C\alpha$$

$$[AB] = C(1-\alpha)$$

Where [AB] represents the concentration of undissociated molecule. On substituting these values in equation 9.23, we get

$$K_a = \frac{(C\alpha)\,(C\alpha)}{C(1-\alpha)}$$

$$K_a = \frac{C\alpha^2}{1-\alpha} \qquad (9.24)$$

Equation (9.24) is the mathematical representation of the Ostwald's dilution law. The equilibrium constant K_a for reactions involving ions is called the ionization constant or dissociation constant of the electrolyte.

It is a constant at a given temperature. If one mole of the electrolyte is dissolved in a volume V dm^3 of the solution, then

$$V = \frac{1}{C} \qquad \text{(V is called the dilution of the solution)}$$

Therefore, equation (9.24) can also be written as

$$K_a = \frac{\alpha^2}{(1-\alpha)V} \qquad (9.25)$$

Equation (9.25) which represents the variation of degree of dissociation with dilution is known as the *Ostwald's Dilution Law.*

In case of weak electrolytes, the value of α is negligibly small as compared to unity so that $1 - \alpha \sim 1$. Therefore equation 9.25 becomes

$$\frac{\alpha^2}{V} = K_a$$

or $$\alpha = (K_a\, V)^{1/2}$$

or $$\alpha \propto (V)^{1/2} \qquad (\because \quad K_a = \text{constant})$$

In other words, the degree of dissociation for weak electrolytes is directly proportional to the square root of dilution.

Experimental Verification of the Dilution Law

The Ostwald's Dilution Law can be experimentally tested by substituting the value of α of a binary electrolyte at different dilutions (V) in the expression.

$$K_a = \frac{\alpha^2}{(1-\alpha)V}$$

and thus calculating the value of K_a. If K_a comes out to be constant, the law is verified. It was found that the law is valid only for weak electrolytes (mainly acids and bases) in dilute solutions.

The degree of dissociation α is best determined by the expression

$$\alpha = \frac{\Lambda}{\Lambda_0} = \frac{\Lambda}{\lambda_+^0 + \lambda^0}$$

Where Λ is the equivalent conductivity at dilution V and Λ_0 is that at infinite dilution. Λ and Λ_0 can easily be determined by conductivity measurements and Kohlrausch's law of ionic mobilities respectively.

Table 9.3 shows the results for acetic acid obtained at 298 K.

Table 9.3 Ionization of Acetic Acid in Aqueous Solution at 298°K
($\Lambda_0 = 390.71 \times 10^{-4}$ S m^2 eqiv^{-1})

Concentration (mol dm^{-3})	Λ (Sm^2 eqiv^{-1}) × 10^4	$\alpha = \frac{\Lambda}{\Lambda_0}$	$K_a = \frac{C\alpha^2}{(1-\alpha)}$
0.505	2.211	0.0057	1.65×10^{-5}
0.186	3.804	0.0098	1.81×10^{-5}
0.093	5.360	0.0138	1.80×10^{-5}
0.040	8.390	0.0216	1.92×10^{-5}

Table 9.3 shows that the value of K_a at different concentrations is almost constant. However, the law fails completely when applied to strong electrolytes like HCl, NaOH, etc.

Example 9.3

The equivalent conductivity of a 0.505 M solution of acetic acid is 2.211×10^{-4} S m^2 eqiv^{-1} at 298 K, while its equivalent conductivity at infinite dilution is 390.71×10^{-4} S m^2 eqiv^{-1}. Calculate the ionization constant of acetic acid.

Solution

Here $\Lambda = 2.211 \times 10^{-4}$ S m^2 eqiv^{-1}

$\Lambda_0 = 390.71 \times 10^{-4}$ S m^2 eqiv^{-1}

and $C = 0.505$ mol dm^{-3}

$$\alpha = \frac{\Lambda}{\Lambda_0} = \frac{2.211 \times 10^{-4}}{390.71 \times 10^{-4}} = 0.0057$$

Applying Ostwald's dilution law in case of acetic acid dissociating as

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

$$K_a = \frac{C\alpha^2}{1 - \alpha}$$

$$= \frac{(0.505)\,(0.0057)^2}{1 - 0.0057}$$

$$= 1.65 \times 10^{-5}$$

9.14 THEORY OF STRONG ELECTROLYTES

The conductance of solution of given electrolyte depends on two factors, namely, the number of ions and their speeds. If the electrolyte is completely dissociated, it is called *strong electrolyte* and if it dissociates partially, it is called *weak electrolyte*. With regard to the conductances of both weak and strong electrolytes, it was observed that the equivalent/molar conductance decreases with increase in concentration. Why?

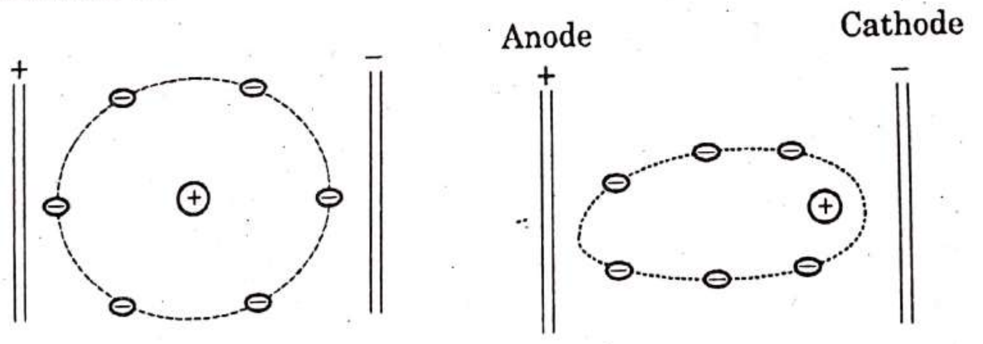
The decrease in equivalent conductance with increase in concentration for weak electrolytes can be explained as due essentially to a decrease in the degree of ionization. Degree of ionization decreases with increase in concentration. With decrease in the degree of ionization, the number of ions per unit volume decreases and this results in the decrease in the equivalent conductance. However, such an explanation cannot apply to strong electrolytes, since these are almost completely dissociated in all dilute solutions. Consequently, to account for the variation of equivalent conductance with concentration in strong electrolytes, some other explanation must be sought, and this is found in the Debye-Huckel-Onsager Theory of conductance.

In 1923, P. Debye and E. Huckel put forward a theory of interionic attraction for dilute solutions of strong electrolytes. This theory occupies a dominant place in all consideration involving electrolytes and their kinetic and thermodynamic behaviour. Debye and Huckel suggested that strong electrolytes exist in solutions as ions. They believe that strong electrolytes at least in dilute solutions are completely ionized and the effect observed is due to unequal distribution of ions resulting from interior attraction. Debye and Huckel showed that, because of the electrostatic attraction between charged ions, each positive ion in the solution must be surrounded on an average with more negative ions than ions of like charge; and conversely, each negative ion must be surrounded on an average with more positive than negative ions. In other words, each ion in the solution is surrounded by *ionic atmosphere whose net charge is opposite to that of the central ion*. They showed, further, that the properties of an electrolyte are determined by the interaction of the central ion with its atmosphere. Since the nature of the atmosphere is determined by the valencies of the ions in the solution, their concentration, the temperature and dielectric constant of the medium, it must follow that these are also the factors controlling the thermodynamic properties of the electrolyte. At any given temperature and in a given solvent, the temperature and dielectric constant are fixed, hence the properties of an electrolyte depend only on the charges of the ions and their concentration not at all on the nature of each electrolyte. These conclusions are only valid for dilute solutions.

According to Debye-Huckel theory of interionic attraction, each ion in solution is surrounded by an ionic atmosphere of opposite ions whose net charge is on the average opposite to that of the central ion. This ionic atmosphere is spherical and symmetrical in nature in the absence of any disturbing factor such as the application of potential across the two electrodes immersed in the solution during the conductance measurement. However, when potential is applied, the ions start moving towards the respective electrodes and as a result the ionic atmosphere is distorted which results in a decrease in the speed of the ions. Debye and Huckel showed that these affects are due to two factors, namely, (i) Asymmetric or Relaxation effect and (ii) Electrophoretic effect.

(i) Asymmetric or Relaxation Effect

According to Debye-and Huckel theory each ion in the solution of an electrolyte is surrounded by an ionic atmosphere of oppositely charged ions. For example, a positively charged ion is surrounded by atmosphere of negatively charged ions and vice versa. When the ions have no external force applied on them, this atmosphere is spherically and symmetrically distributed about the ion. However, when an external force is imposed, as when a potential is applied across the two electrodes, the ions present in the solution move towards their respective electrodes. The central +ve ion will tend to move towards *cathode*, while its negatively charged ion atmosphere will move towards *anode*. As a result, the symmetry of the ionic atmosphere about central ion is destroyed. As long as the ionic atmosphere is symmetrical: it will exert uniform force of attraction on the central ion from all possible directions and the net effect will be nil. (Fig.9.4(a))



(a) Symmetrical ionic atmosphere (No field)

(b) Asymmetric ionic atmosphere (Electric field)

Fig.9.4 Asymmetric effect showing distribution of ionic atmosphere in the pressure of an applied field

But in case of distorted ionic atmosphere a shown in Fig. 9.4(b), the of force attraction from the rear becomes prominent on the moving central ion. Therefore, the central moving ion experiences a backward pull or a retarding force. Its mobility is slowed down and hence, the effective conductance of the solution decreases. This backward pull on the central ion is known as *asymmetric effect* as it is due to the lack of symmetry in the ionic atmosphere. Once the ionic atmosphere is destroyed, a finite time is required for rebuilding another symmetric ion-atmosphere. This time is called relaxation time. This time of relaxation is considered to explain the retardation in the motion of the central moving ion by the ionic atmosphere, therefore asymmetric effect is also known as *relaxation effect*.

(ii) Electrophoretic Effect

In addition to the asymmetric effect, there is another factor with retards the mobility of ion, the electrophoretic effect. This effect arises from the fact that an ion, in moving through the solution, does not travel through a stationary medium, but through one that moves in a direction opposite to that of the ion. Ions are generally solvated, and when these move, they carry with them solvent. Any +ve ion migrating towards the cathode, has, then, to thread (pass into) its way through the medium moving with negative ions towards anode. Similarly –ve ions have to migrate through the molecules of solvent carried by +ve ions in the opposite direction. These counter movements have a retarding influence on the mobility of the central ion. This effect is known as electrophoretic effect. This causes an additional viscous force which further slows down the speed of the ions and hence the conductance.

It is called electrophoretic effect because it is somewhat analogous to that opposing the movement of colloidal particles in the electric field. It slows down the speed of the ions in the same way as swimming against the current in a river would slow down a swimmer. For any dilute solution, the ionic atmosphere is almost non-existent, so asymmetric effect is zero. Similarly at infinite dilution, the electrophoertic effect is also negligible, but both effects have definite values in concentrated solutions. Debye and Huckel showed that both of these retarding effect on an ion produce a decrease in the equivalent conductance. These are the theoretical explanation for the decrease of equivalent conductance in case of solutions of strong electrolytes.

9.15 DEBYE-HUCKEL THEORY: THE IONIC ATMOSPHERE

The possibility that the attractive forces between ions might have some influence on the electrolytic conductance, especially with strong electrolytes, was considered by Noyes (1904), Sutherland (1906) Bijerum (1909) and Miller (1912) among others. But the modern quantitative treatment of this concept is due mainly to the work of Debye and Huckel and its extension chiefly by Onsager and Falkenhagen.

When an electrolyte is dissolved in a polar solvent, it gets dissociated into ions and the solutions may contain a large number of kinetically identifiable species in addition to the solvent molecules which are always in equilibrium with each other. A completely random distribution of ions around each other can not be physically possible. A positive ion will have a negative ion in its immediate vicinity, thereby, resulting in an ordered arrangement, which is offset by thermal motions. Thus the resulting situation is a dynamic compromise between the electrostatic interactions and kinetic collisions. The net result is that in a small volume element of the solution around an ion, on time average, there is slightly greater concentration of the ions carrying opposite charge than those carrying similar charge. Thus, each ion has an ionic atmosphere of oppositely ions, whose net electrical charge is equal and opposite to that of the central ion. This forms an essential postulate of the Debye-Huckel theory for dilute solutions of strong electrolytes.

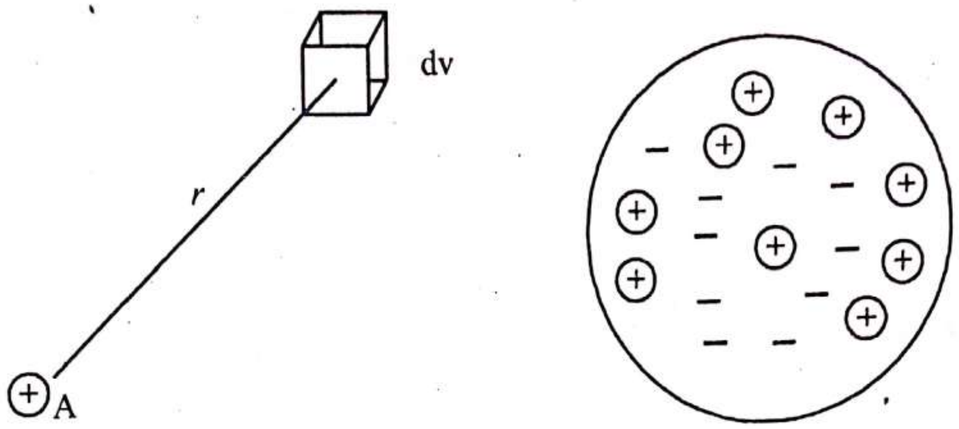


Fig. 9.5 The ionic atmosphere and time average distribution of ions around a reference ion

Let us consider a positive ion situated at A(Fig.9.5). Suppose there is small volume element dv at the end of radius vector r; the distance r is supposed to be of the order of less than about 100 times, as the diameter of the ion. Due to thermal movement of ions sometimes there occurs an excess of positive ions and sometimes an excess of negative ions in the volume dv. If a time average is taken, however, it will be found to have, as a consequence of electrostatic attractions by the positive charge at A, a negative charge density. In this way every ion may be assumed to have an ionic atmosphere of opposite sign. The net charge of the ionic atmosphere is equal in magnitude and opposite in sign to that of the central ion. It is possible to define the effective thickness of the ionic atmosphere.

Debye and Huckel took the interionic attraction into consideration and calculated the ratio of activity to the concentration of an ion in dilute solutions. Suppose the time average of the electrical potential in the center of the volume element dv in Fig.9.5 is Ψ. It is defined as the work done in bringing a unit charge from infinity to a particular point. The work done in bringing a positive ion of valence Z_+ and carrying a charge ϵ to that point is given by $Z_+\epsilon\Psi$. Similarly the work done in bringing a negative ion is $Z_-\epsilon\Psi$. Z_+ and Z_- are numerical values only, and do not include the sign. If the concentrations of the ions at a considerable distance from the given ion, where Ψ may be taken as zero, are n_+^o and n_-^o per unit volume, then by the Boltzmann distribution law for particles in a filed of varying potential, the concentration of the positive and negative ions, i.e., n_+ and $n-$, at the point under consideration, are given by

$$n_+ = n_+^o \, e^{-(Z_+\epsilon\Psi/kT)} \tag{9.26}$$

and $$n_- = m_-^o \, e^{-(Z_-\epsilon\Psi/kT)} \tag{9.27}$$

where k is the Boltzmann constant. Since Z_+ and Z_- are the numerical values only, it is clear that n_- is greater than n_+, and so there are on the average more negative ions than positive ions in the vicinity of any positive ion, the reverse will be true for negative ion. It is seen, therefore, that every ion is surrounded by an oppositively charged ionic atmosphere.

In the vicitinity of A^+, the density of electricity or electrical charge density (ρ) at any point is equal to the excess positive or negative electricity per unit volume at that point, that is,

$$\rho = n_+ Z_+ \in - n_- Z_- \in$$

$$\rho = \in[n_+ Z_+ e^{-(Z_+ \in \Psi/kT)} - n_- Z_- e^{-(-Z_- \in \Psi/kT)}] \qquad (9.28)$$

For uni-univalent electrolyte, Z_+ and Z_- are unity and n_+ and n_- must be equal because of electrical neutrality hence, Eq.(9.28) reduces to

$$\rho = \in(ne^{-\in\Psi/kT} - ne^{\in\Psi/kT})$$

or $$\rho = \in n(e^{-\in\Psi/kT} - e^{\in\Psi/kT}) \qquad (9.29)$$

or $$\rho = \in n(e^{-x} - e^{x}) \qquad (9.30)$$

where n is the number of either kind of ion in unit volume. Expanding the two exponential series and writing x in plane of $\in\Psi/kT$, one gets,

$$e^x = 1 + \frac{X}{1!} + \frac{X^2}{2!} + \frac{X^3}{3!} + \ldots$$

$$e^{-x} = 1 - \frac{X}{1!} + \frac{X^2}{2!} - \frac{X^3}{3!} + \ldots$$

$$-e^x = -1 - \frac{X}{1!} - \frac{X^2}{2!} - \frac{X^3}{3!} \ldots$$

$$(e^{-x} - e^x) = 1 - \frac{X}{1!} + \frac{X^2}{2!} - \frac{X^3}{3!} \ldots - 1 - \frac{X}{1!} - \frac{X^2}{2!} - \frac{X^3}{3!} \ldots \infty$$

$$(e^{-x} - e^x) = -\frac{2X}{1!} - \frac{2X^3}{3!} - \frac{2X^5}{5!} - \ldots \infty$$

$$(e^{-x} - e^x) = \frac{-2X}{1!}\left(1 + \frac{X^2}{3!} + \frac{X^4}{5!} + \ldots\right)$$

$$\rho = \in n\left(-\frac{2\in\Psi}{kT}\right)\left[1 + \frac{X^2}{3!} + \frac{X^4}{5!} + \ldots\right]$$

or $$\rho = -\frac{\in^2\Psi}{kT} 2n \left(1 + \frac{X^2}{3!} + \frac{X^4}{5!} + \ldots\right) \qquad (9.31)$$

If it is assumed that X is small in comparison with unity, all terms beyond the first in the parenthesis may be neglected

$$\rho = -\frac{\in^2\Psi}{kT} 2n \qquad (9.32)$$

where $2n = Z_+^2 n + Z_-^2 n$

$$2n = n_+Z_+^2 + n_-Z_-^2$$

This is only true for 1 : 1 electrolyte. Hence Eq.(9.32) may be written as

$$\rho = -\frac{\epsilon^2\Psi}{kT}(n_+Z_+^2 + n_-Z_-^2) \tag{9.33}$$

In the general case where Z+ and Z– are not necessarily unity and if the solution may contain several kinds of the ions, Eq.(9.33) may take the following form.

$$\rho = -\frac{\epsilon^2\Psi}{kT}\sum_i n_i Z_i^2 \tag{9.34}$$

Where n_i and Z_i represent the number per unit volume and valence of the ions of i^{th} kind. The summation is taken over all kinds of ions present in the solution and Eq.(9.34) is applicable irrespective of the number of different kinds of ions.

In order to solve for Ψ it is necessary to have another relationship between ρ and Ψ and this may be obtained by intorducing Poisson's equation and this equation in rectangular coordinates is

$$\frac{\partial^2\Psi}{\partial x^2} + \frac{\partial^2\Psi}{\partial y^2} + \frac{\partial^2\Psi}{\partial z^2} = -\frac{4\pi\rho}{D} \tag{9.35}$$

Where x, y and z are the coordinates of the point in the given volume element and D is the dielectric constant of the medium. Converting to polar coordinates, and making use of the fact that the terms containing $\partial\Psi/\partial\theta$ and $\partial\Psi/\partial\phi$ will be zero, since the distribution of the potential about any point in the electrolyte must be spherically symmetrical and consequently, independent of the angles θ and ϕ, Eq.(9.35) becomes

$$\frac{1}{r^2}\cdot\frac{d}{dr}\left(r^2\frac{d\Psi}{dr}\right) = -\frac{4\pi\rho}{D} \tag{9.36}$$

Substituting the value of ρ from Eq.(9.34) in Eq.(9.36) we get

$$\frac{1}{r^2}\cdot\frac{d}{dr}\left(r^2\frac{d\Psi}{dr}\right) = -\frac{4\pi}{D}\left(-\frac{\epsilon^2\Psi}{kT}\Sigma n_i Z_i^2\right)$$

$$\frac{1}{r^2}\cdot\frac{d}{dr}\left(r^2\frac{d\Psi}{dr}\right) = \frac{4\pi\epsilon^2\Psi}{DkT}\sum_i n_i Z_i^2$$

$$\frac{1}{r^2}\cdot\frac{d}{dr}\left(r^2\frac{d\Psi}{dr}\right) = k^2\Psi \tag{9.37}$$

where the quantity k(not to be confused with specific conduction) is defined by

$$k^2 = \frac{4\pi\epsilon^2\sum_i n_i Z_i^2}{DkT}$$

$$\text{or} \qquad k = \left(\frac{4\pi \in^2 \sum_i n_i Z_i^2}{DkT} \right)^{1/2} \tag{9.38}$$

where r denotes the distance from the central ion to the point where Ψ is determined, and $\frac{1}{k}$ has the dimensions of length. It is called Debye-Huckel reciprocal length. It is the distance over which electrostatic field of an ion extends with appreciable strength. k^{-1} is a measure of the thickness of the ionic atmosphere.

The differential equation Eq.(9.37) can be solved, and the solution has the general form

$$\Psi = \frac{Ae^{-kr}}{r} + \frac{Be^{kr}}{r} \tag{9.39}$$

Where A and B are integration constants, whose values are determined by applying the boundary conditions. Since Ψ must approach zero as r increases, because the potential at infinite distance from the given point in the solution must be zero

$$0 = \frac{A\,e^{-\infty}}{\infty} + \frac{B\,e^{\infty}}{\infty}$$

$$0 = 0 + \frac{B\,e^{\infty}}{\infty}$$

$$e^{\infty} = \infty$$

$$e^{-\infty} = 0$$

$$\frac{1}{e^{\infty}} = 0$$

This can be only true if B = 0, since $\frac{e^{\infty}}{\infty} \neq 0$, hence Eq.(9.39) becomes

$$\Psi = \frac{A\,e^{-kr}}{r} \tag{9.40}$$

The value of A can be calculated by the fact that for very dilute solution $\sum_i n_i Z_i^2$ is almost zero and hence k is also zero. The value of potential Ψ_i at the point under consideration will be

$$\Psi_i = \frac{A}{r} \tag{9.41}$$

In case of dilute solutions the potential in the neighbourhood of an ion will be due to that ion alone, since other ions are too far away to have any influence. If the ion is being regarded as being a point charge, the potential at small distance will be

$$\Psi_i = \frac{Z_i \in}{Dr} \tag{9.42}$$

Eliminating Ψ_i between Eq.(9.41) and Eq.(9.42), we get

$$\frac{A}{r} = \frac{Z_i \in}{Dr}$$

or $$A = \frac{Z_i \epsilon}{D} \qquad (9.43)$$

Substituting the value of A into Eq. (9.40), we get

$$\Psi = \frac{Z_i \epsilon}{Dr} e^{-kr} \qquad (9.44)$$

The value of Ψ represented by Eq.(9.44) is the mean value of the potential at point r produced by the ionic atmosphere and the central ion. Real solutions are characterized by the potential of the ionic atmosphere which is found as the difference between Ψ and Ψ_i

$$\Psi_{ia} = \Psi - \Psi_i$$

$$\Psi_{ia} = \frac{Z_i \epsilon}{Dr} e^{-kr} - \frac{Z_i \epsilon}{Dr}$$

$$\Psi_{ia} = \frac{Z_i \epsilon}{Dr} (e^{-kr} - 1)$$

$$\Psi_{ia} = \frac{Z_i \epsilon}{Dr} (-kr)$$

$$\Psi_{ia} = -\frac{Z_i \epsilon\, k}{Dr} \qquad (9.45)$$

$$\therefore \; e^{-kr} = 1 - kr$$

$$1 - e^{-kr} = [1 - ka] = kr$$

$$e^{-kr} - 1 = 1 - kr - 1 = -kr$$

The Eq.(9.45) is independent of r and hence it may be assumed to hold even when r is zero, so that the potential on the ion itself, due to ionic atmosphere is given by above equation. The net charge of the ionic atmosphere is $-Z_i\epsilon$, because it is equal in magnitude and opposite in sign to that of the central ion itself. If this charge was placed at a distance 1/k from the ion, the potential produced at it, would be $-Z_i\epsilon k/D$, which is identical with the value given by equation (9.45). The quantity 1/k can thus be regarded as a measure of the thickness of the ionic atmosphere in a given solution. According to the definition of k, the thickness of the ionic atmosphere will depend on the number of ions of each kind present in unit volume and on their valence. If C_i is the concentration of the ions of the i^{th} kind expressed in moles (gram-ions) per liter, then

$$n_i = C_i \frac{N}{1000}$$

where N is the Avogadro number, hence from Eq.(9.38)

$$\frac{1}{k} = \left(\frac{DT}{\Sigma C_i Z_i^2} \frac{1000\, k}{4\pi \epsilon^2 N} \right)^{1/2}$$

The value of universal constants are as follows: *k* is 1.38 × 10^{-16} erg per degree, ∈ is 4.80 × 10^{-10} esu and N is 6.025 × 10^{23}, hence

$$\frac{1}{k} = 2.81 \times 10^{-10} \left(\frac{DT}{\Sigma C_i Z_i^2} \right)^{1/2} \text{cm}$$

For water as solvent at 25°C, D is 78.6 and T is 298, so that

$$\frac{1}{k} = \frac{4.31 \times 10^{-8}}{(\Sigma C_i Z_i^2)^{1/2}} \text{ cm}$$

The thickness of the ionic atmosphere is thus seen to be of the order of 10^{-8} cm or 10^{-10} m. It decreases with increasing concentration and valence of the ions present in the electrolyte, and increases with increasing dielectric constant of the solvent and with increasing temperature.

9.16 DEBEY-HUCKEL-ONSAGER'S EQUATION

According to Debye-Huckel theory of strong electrolytes each ion is surrounded by an ionic atmosphere of opposite charge. A moving ion under the influence of applied electrical field is un-symmetrically surrounded by the ionic atmosphere of opposite charge. The charge density is greater in the rear than in the front of ion. As the ionic atmosphere is not symmetrical, it results in the retardation of the ion moving under the influence of applied field. This influence on the speed of ion is called asymmetric or relaxation effect. A viscous resistance of the solvent also acts on the moving ion. It is similar to the resistance acting against the movement of the colloidal particles in an electric field. It is called electrophoretic effect Both asymmetric and electrophoretic effects retard the speed of the central moving ions and ultimately decrease the conductance.

Debye and Huckel made an attempt to calculate the magnitude of the process which oppose the motion of the ions in solution. They supposed the ions to travel through the solution in straight lines, neglecting the zigzag Brownian motion brought about by the collisions of surrounding solvent molecules. This theory was improved in 1926 by the Norwegian-American physical chemist Lars Onsager (1903-1976) who took Brownian motion into account. They applied Stockes's law and derived the following expression for electrophoretic effect for an ion of the ith kind.

$$\text{Electrophoretic force} = \frac{\in Z_i k\, K_i V}{6\pi\eta} \tag{9.46}$$

Where K_i is the coefficient of frictional resistance of the central ion with reference to the solvent, η is the viscosity of the medium, V is the applied potential gradient, $\in$ is the electronic charge, Z_i is the valence of the i^{th} ion, k is the reciprocal of the thickness of the ionic atmosphere. The same result was derived in an attractive manner by Onsager, who showed that it is not necessary for the Stokes's law to be strictly applicable in the immediate vicinity of an ion.

In the first derivation of the relaxation force Debye and Huckel did not take into account the natural Brownian movement of the ions but Onsager also considered this movement for the derivation of relaxation force. According to Onsager.

$$\text{Relaxation force} = \frac{\epsilon^3 Z_i k}{6DkT} wV \qquad (6.47)$$

Where D is the delectric constant of the medium, k is Boltzmann constant, T is the absolute temperature K is same as in previous equation, Z_i is the value of the ion, V is the applied potential and w is defined as

$$w = z_+ z_- \frac{2q}{1+q^{1/2}}$$

$$\text{When } q = \frac{z_+ z_-}{z_+ + z_-} \; \frac{\lambda_+ + \lambda_-}{z_+\lambda_- + z_-\lambda_+} \qquad (9.41)$$

λ_+ and λ_- are the ionic conductance's of +Ve and –Ve ions.

Let us suppose that an ion of ith kind is moving through a solution with a steady velocity Ui. The driving force acting an the ion of ith kind due to applied electrical field is

$$\text{Driving force} = \epsilon Z_i V \qquad (9.49)$$

It is now possible to equate the forces acting on anion of ith kind when it is moving through a solution with a steady velocity; the driving force due to applied electrical field is opposed by the frictional force of the solvent (K_iU_i), together with the electrophoretic and relaxation forces hence.

$$\epsilon Z_i V = K_i U_i + \frac{\epsilon Z_i k}{6\pi\eta} K_i V + \frac{\epsilon^3 Z_i k}{6DkT}.wV$$

dividing throughout by K_iV and rearranging, we get

$$\frac{\epsilon Z_i}{K_i} = \frac{U_i}{V} + \frac{\epsilon Z_i k}{6\pi\eta} + \frac{\epsilon^3 Z_i k}{6DkT}.\frac{w}{K_i}$$

$$\text{or} \qquad \frac{Ui}{V} = \frac{\epsilon Z_i}{K_i} + \frac{\epsilon Z_i k}{6\pi\eta}.\frac{\epsilon^3 Z_i k}{6DkT}.\frac{w}{K_i}$$

Multiply the above equation throughout by V

$$U_i = \frac{\epsilon Z_i V}{K_i} - V\left(\frac{\epsilon Z_i k}{6\pi\eta} + \frac{\epsilon^3 Z_i k}{6DkT}.\frac{w}{K_i}\right)$$

$$Ui = \frac{\epsilon Z_i V}{K_i} - V \epsilon k\left(\frac{Z_i}{6\pi\eta} + \frac{\epsilon^2 Z_i}{6DkT}.\frac{w}{K_i}\right) \qquad (9.50)$$

If the potential gradient is taken as one volt per cm

$$\therefore \qquad 1\ \text{volt}/\text{cm} = \frac{1}{300}\,\text{esu}$$

Since the forces of attraction are electrostatic in nature.

$$U_i = \frac{\in Z_i}{300 K_i} - \frac{\in k}{300}\left(\frac{Z_i}{6\pi\eta} + \frac{\in^2 Z_i}{6\,DkT}\cdot\frac{w}{K_i}\right) \qquad (9.51)$$

At infinite dilution k is zero, so the above equation reduces to

$$U_i = \frac{\in Z_i}{300 K_i} \qquad (9.52)$$

But $U_i^o F = \lambda_i^o$ so $U_i^o = \frac{\lambda_i^o}{F}$

Hence $$\frac{\lambda_i^o}{F} = \frac{\in Z_i}{300 K_i} \qquad (9.53)$$

Since ions behave independently at infinite dilution, therefore ionic conductance at infinite dilution can be written as according to Kohlrausch's law $\lambda_+^o = FU_+^o$ and $\lambda_-^0 = FU_-^0$

Again we know that $U_i = \frac{\lambda_i}{\alpha F}$

When α is the degree of dissociation. Substituting the value of U_i and U_i^o into Eq. (9.51), we get

$$\frac{\lambda_i}{\alpha F} = \frac{\lambda_i^o}{F} - \frac{\in k}{300}\left(\frac{Z_i}{6\pi\eta} + \frac{\in^2 Z_i}{6\,DkT}\cdot\frac{w}{K_i}\right) \qquad (9.54)$$

When the electrolyte is fully ionized, i.e. $\alpha = 1$, then

$$\lambda_i = \lambda_i^o - \frac{\in k}{300}\left(\frac{Z_i F}{6\pi\eta} + \frac{\in^2 Z_i F}{6\,DkT}\cdot\frac{w}{K_i}\right) \qquad (9.55)$$

We know that $\frac{\lambda_i^o}{F} = \frac{\in Z_i}{300 K_i}$

$\therefore \quad \lambda_i^o\, 300\, K_i = \in Z_i F$

Substituting this value in above equation we get

$$\lambda_i = \lambda_i^o - \frac{\in k}{300}\left(\frac{Z_i F}{6\pi\eta} + \frac{\in 300 \lambda_i^o}{6\,DkT}.w\right) \qquad (9.56)$$

But $$k = \left(\frac{4\pi \in^2}{DkT}\sum_i n_i Z_i^2\right)^{1/2} \qquad \text{(cf Eq.9.38)}$$

Where n_i is the number of ions present for unit volume. Substituting this value in Eq. (9.56), we get.

$$\lambda_i = \lambda_i^o - \frac{\epsilon}{300}\left(\frac{4\pi\epsilon^2}{DkT}\sum_i n_i Z_i^2\right)^{1/2}\left(\frac{Z_iF}{6\pi\eta} + \frac{300\epsilon\lambda_i}{6DkT}.w\right)$$

$$\lambda_i = \lambda_i^o - \frac{\epsilon}{300}\left(\frac{4\pi\epsilon^2 N}{DkT\times 1000}\sum c_i Z_i^2\right)^{1/2}\left(\frac{Z_iF}{6\pi\eta} + \frac{300\epsilon\lambda_i^o w}{6DkT}\right)$$

Here $ni = \frac{CiN}{1000}$

The values of universal constant are as follows: k is 1.38×10^{-16} erg per degree ϵ is 4.802×10^{-10} csu and N is 6.025×10^{23}, hence.

$$\lambda_i = \lambda_i^o - \left[\frac{29.15Zi}{(DT)^{\frac{1}{2}}\eta}\left(\sum ciZi^2\right)^{\frac{1}{2}} + \frac{9.9\times10^5}{(DT)^{\frac{3}{2}}}\lambda_i^o w\left(\sum ciZi^2\right)^{\frac{1}{2}}\right]$$

$$\lambda_i = \lambda_i^o - \left[\frac{29.15Zi}{(DT)^{\frac{1}{2}}\eta} + \frac{9.9\times10^5}{(DT)^{\frac{3}{2}}}\lambda_i^o w\right]\left(\sum ciZi^2\right)^{\frac{1}{2}} \qquad \text{—9.57}$$

For 1:1 electrolyte. $C_i = C_+ + C_-$, $Z_i = Z_+ + Z_-$

$$\lambda_i = \lambda_i^o - \left[\frac{29.15(Z_+ + Z_-)}{(DT)^{\frac{1}{2}}\eta} + \frac{9.9\times10^5}{(DT)^{\frac{3}{2}}}\lambda_i^o w\right](C_+Z_+^2 + C_-Z_-^2)^{\frac{1}{2}}$$

The quantities C_+ and C_- represent the concentrations of the ions in moles per liter, then may be replaced by the corresponding concentrations C in equivalent for liter, where C is the same for both ions i.e. $C_+ = C_- = C$

$$\lambda_i = \lambda_i^o - \left[\frac{29.15(Z_+ + Z_-)}{(DT)^{\frac{1}{2}}\eta} + \frac{9.9\times10^5}{(DT)^{3/2}}\lambda_i^o w\right]\sqrt{C}\,(Z_+^2 + Z_-^2)^{1/2}$$

The equivalent conductance of an electrolyte is equal to the sum of the conductance's of the constitute ions, and so to follows from above equation.

$$\Lambda = \Lambda_o - \left[\frac{29.15(Z_+ + Z_-)}{(DT)^{1/2}\eta} + \frac{9.9\times10^5\Lambda_o w}{(DT)^{3/2}}\right]\sqrt{C}\left(Z_+^2 + Z_-^2\right)^{1/2}$$

For 1:1 electrolyte, $Z_+ = Z_- = 1$ and $w = 2 - \sqrt{2}$, so

$$\Lambda = \Lambda_o - \left[\frac{29.15(Z_+ + Z_-)}{(DT)^{1/2}\eta} + \frac{9.9\times10^5}{(DT)^{3/2}}\Lambda_o\, 2-\sqrt{2}\right]\sqrt{2C}$$

$$\Lambda = \Lambda_o - \left[\frac{82.4}{(DT)^{1/2}\eta} + \frac{8.2\times10^5}{(DT)^{3/2}}\Lambda_o\right]\sqrt{C} \qquad (9.58)$$

$$\Lambda = \Lambda_o - [A + B\,\Lambda_o]\sqrt{C} \qquad (9.59)$$

When A and B are constants dependent upon the nature of solvent and temperature.

$$A = \frac{82.4}{(DT)^{1/2}\eta}$$

and $$B = \frac{8.2\times10^5}{(DT)^{3/2}}$$

Equation (9.58) and (9.59) represents the forms of the Debye Huckel-Onsager conductance equation, these relationships are based on the assumption that the dissociation of the electrolyte is complete. This equation accounts for the falling off of equivalent conductance at appreciable concentrations in terms of decrease in ionic velocity resulting from inter ionic forces. The decrease of conductance due to these forces is represented by the quantities in the square brackets. The first term gives the effect due to electrophoretic force and the second term represents the influence of asymmetric force. It is apparent from the equation that for a given solvent at a definite temperature, the magnitude of the interionic forces increases with increasing valences of the ions and with increasing concentration of the electrolyte.

Validity of Debye-Huckel Onsager Equation:

Assuming complete dissociation of 1:1 electrolyte the D.H.O equation may be written in the form.

$$\Lambda = \Lambda_o - (A + B\Lambda_o)\sqrt{C}$$

Where A and B are constants dependent only on the nature of the solvent and temperature. The above equation is an equation of straight line. In order to test the validity of above equation, the experimental value of Λ of very dilute solution of a strong electrolyte are plotted against $\sqrt{C}$. A straight line is obtained with slope equal to $A + B\Lambda_o$ and intercept Λ_o as shown in Fig-9.6. This equation is obeyed at the concentration of about 2×10^{-3} equivalent per liter. This equation is also applicable to non-aqueous solvents. This equation holds good for certain electrolytes like NaCl, $AgNO_3$, KCl,

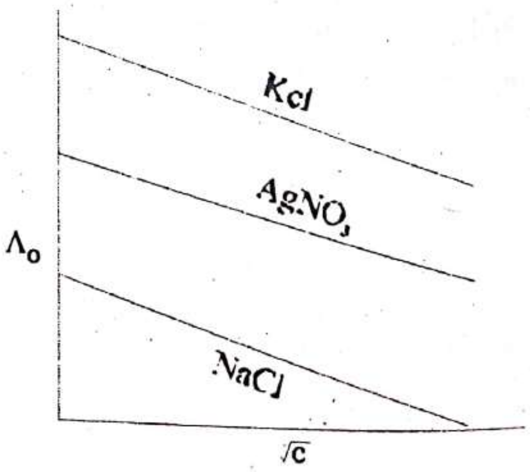


Fig. 9.6. Test of Debye- Huckel-Onsager equation

HCl etc. Marked deviations are observed for 2:2 solutes, and for solutions prepared in solvents having lower dielectric constants. Negative deviations from theoretical values of conductance may be due to incomplete dissociation. It has been observed that smaller ions, possessing higher valence, show marked deviation in a medium of low dielectric constant.

D.H.O. equation also shows deviation of higher concentration of solutes. Bjerrum was the first man who tried to explain this observation. He said that when electrolyte concentration is increased, the ions become close to each other and the forces of attraction between opposite charges are increased. At higher concentration, individual ions, associate into electroneutral ion pairs (B^+A^-) which are unable to conduct electricity. As a result of the combination of charged particles, the conductance decreases.

9.17. WIEN AND DEBYE-FALKENHAGEN EFFECTS

The conductance of completely dissociated electrolytes is independent of the electric field strength in the range of moderate field strengths. At higher field strengths of the order 10^7 Vm^{-1}, however, Wien (1922) observed an increase in the conductance with increasing field strength. The increase is more intense for more concentrated solutions and for polyvalent ions the conductance always approaches a limiting value with increasing field strength. This effect of field strength on the conductance is called *Wien effect*. This effect can easily be interpreted by making use of the ion-ionic atmosphere interaction model. Under condition of high field strength, the ionic mobility is so large that the ionic atmosphere is unable to rearrange itself fully around the moving central ion. Consequently, both the electrophoretic and time-relaxation effects exert no influence on the moving ion, and the observed conductance rises above the value found for low field strength.

A second phenomenon, also observed by Wien under conditions of high field strength, deals with the influence of the electrical field on the dissociation constant of the weak electrolytes. A high field strength affects the dissociation positively and, consequently, affects the equilibrium dissociation constant (dissociation equilibrium constant) of such an electrolyte. The theoretical interpretation of this very important observation, as given by Onsager (1934) and Bass (1968) is based on the fact that at high electrical field strengths the probability of ion-pair and triple-ion formation is much lower than at low field strengths.

If a high frequency alternating current is applied to an electrolyte, and the time of oscillation is equal to or less than the relaxation time of the ionic atmosphere, the asymmetrical charge distribution usually associated with an ion in motion cannot form completely. The retardation of the ionic velocity due to asymmetric effect is thus reduced, and the conductance of the solution should be greater than the normal value P. Debye and H.Falkenhagen (1928) deduced theoretically the existence of high frequency effect on the conductivity of the ion. In 1928 Sach proved experimentally that this is really so at frequencies exceeding 5 MHz, where the equivalent conductance approaches a value some what lower than Λ_α. The value must be lower than Λ_α because the high frequency field eliminates the time relaxation effect only; it has no influence on the electrophoretic effect.

It is important to emphasize that the influence of high frequency currents and high voltages provides strong arguments in favor of the view that under normal conditions ionic velocities, and hence conductances are below those for infinite dilution because of the effect of the ionic atmosphere which increases with increasing concentration.

9.18 IONIC STRENGTH

When we dissolve an electrolyte into aqueous solution, it dissociates into positive and negative ions. When the concentration of the electrolyte increases in the solution, there occurs an interaction between positive and negative ions. Because of this interaction the ions behave differently from those in dilute solutions. The behavior of ions in solution is influenced by a number of factors, chief among which are the natural attraction of ions of unlike charge and repulsion of ions of like charge (Coulomb's law) and the influence of thermal agitation (Boltzmann distribution law) to counteract the electrical attraction and repulsion. The effects are dependent upon the total ionic composition of the solution, which is expressed by G.N. Lewis in a concept called *ionic strength* of the solution. Ionic strength is a useful concept because it allows us to consider some general expressions that depend only on ionic strength and not on the identities of the ions themselves. This quantity is a measure of electrical environment in the solution.

Ionic strength is given the symbol μ and is defined as half the sum of the terms obtained by multiplying the molality (or concentration) of each ionic species present in the solution by the square of its valence; thus

$$\mu = \frac{1}{2} \sum m_i Z_i^2 \tag{9.60}$$

Where m_i is the molality of the ion and Z_i is its ionic charge. The product $m_i z_i^2$ is summed for all the ions in the solution then divided by two to give the ionic strength.

If a solution contains a number of ionic species indicated by the subscripts 1,2,3, etc. so that their respective molalities are m_1, m_2, m_3, etc. in gram ions per 1000 gram of solvent, and Z_1 Z_2 an Z_3 etc. are the corresponding valencies, then the ionic strength is given by

$$\mu = \frac{1}{2}\left(m_1 Z_1^2 + m_2 Z_2^2 + m_2 Z_3^2 + \dots\right) \tag{9.61}$$

For a single electrolyte such as sodium chloride or potassium sulfate, the above equation reduces to two terms, one for positive and one for negative ion, viz.

$$\mu = \frac{1}{2}(m_+ Z_+^2 + m_- Z_-^2) \tag{9.62}$$

When m_+ and m_- are the molalities and Z_+ and Z_- are the valences of positive and negative ions. Ionic strength is an empirical relationship and is expressed in terms of molal concentration of the ions rather than in SI unit of ions per cubic meter.

For uni-univalent electrolyte such as NaCl or KCl of molality m, the ionic strength is equal to its molality.

$$\mu = \frac{1}{2}(m \times 1^2 + m \times 1^2)$$

$$\mu = \frac{2m}{Z} = m$$

Thus for 1:1 electrolyte μ is equal to its m. One should remember that ionic strength is a property of the solution and not of any particular ion.

Example 9.4

Calculate the ionic strength of (i) 0.1 molal NaCl (ii) 0.2 molal K_2SO_4 (iii) a solution containing 0.1 m KCl and 0.2 m K_2SO_4 (iv) 0.2 m $BaCl_2$ solution.

Solution:

(i) $m_+ = m_- = 0.1$. $Z_+ = Z_- = 1$. so

$$\mu = \frac{1}{2}(0.1 \times 1^2 + 0.1 \times 1^2)$$

$$\mu = 0.1$$

(ii) K_2SO_4 produces two K^+ ions and one SO_4^{2-} ion

$m_+ = 2 \times 0.2 = 0.4$. $Z_+ = 1$

$m_- = 0.2$ $Z_- = 2$

$$\mu = \frac{1}{2}(0.4 \times 1^2 + 0.2 \times 2^2)$$

$$= 0.6$$

(iii) In a mixture of solution containing 0.1m KCl and 0.2m K_2SO_4.
Total molality of K^+ ion = $m_1 = 0.1 + 0.4 = 0.5$

molality of Cl^- ion = $m_2 = 0.1$

molality of SO_4^{2-} ion = $m_3 = 0.2$

$$\mu = \frac{1}{2}(m_1 z_1^2 + m_2 z_2^2 + m_3 z_3^2)$$

$$= \frac{1}{2}(0.5 \times 1^2 + 0.1 \times 1^2 + 0.2 \times 2^2)$$

$$= 0.7$$

(iv) $BaCl_2$ produces one Ba^{2+} ion and two Cl^- ions

$m_+ = 0.2$, $Z_+ = 2$

$$m_- = 2 \times 0.2 = 0.4,\ Z_- = 1$$

$$\mu = \frac{1}{2}(0.2 \times 2^2 + 0.4 \times 1^2)$$

$$= 0.6$$

9.19. ACTIVITIES AND ACTIVITY COEFFICIENTS OF STRONG ELECTROLYTES:

The thermodynamic and other properties of the solutions of non-electrolytes can be adequately expressed in terms of their concentrations, even at moderate concentrations. But the solutions of electrolytes exhibit marked deviation even at relatively low concentrations. Dilute ionic solutions have concentration of 0.001 m or even less. According to Debye-Huckel theory of interionic attraction, the electrostatic attractions between the ions in the solution of an electrolyte have significant influence on the mobility of ions. The ionic concentrations in case of weak electrolytes, being low do not show appreciable deviation from the ideal behavior. But in solutions of strong electrolytes the ionic concentrations are large, so interionic forces cannot be neglected. Due to electrostatic attraction between fractions of cations and anions, the solution exhibits the properties of one in which the effective or apparent concentrations of the ions are less than the theoretical concentrations. Depending on the relative importance of factors, such as ion-ion attractions and ion-solvent interactions, the effective concentration of the solute dissolved in water may appear to be less than, equal to or greater than the molal concentration. This effect becomes more significant at higher concentrations and increasing valence of the ions.

G.N. Lewis suggested due to restricted, mobility of the ions in solutions of strong electrolytes the ions do not exert their *full effect* for showing their behavior. He proposed the term activity in place of concentration term (molarity, molality, formality, mole fraction), so as to explain the departure of electrolyte solution from ideal behavior. To distinguish between molar or molal or formal concentration of a substance and the effective concentration of a substance which accounts non-ideal behavior, the latter is called the activity of the species. So the effective concentration of an ion in a solution is called its *activity*. It is customary to relate the activity of a species to its concentration through the expression.

$$a_i = \gamma_i m_i \tag{9.63}$$

in which a_i is the activity of the substance *i*, γ_i, is the activity coefficient of the substance *i* and m_i is the molal concentration of the substance *i*. Activity coefficient (γ) is not a constant and its value varies with the concentration. For aqueous solutions, both activity and concentration are expressed in the same units, so that the activity coefficient is dimensionless. [For dilute solutions, the molarity is almost numerically equal to molality, which is preferred unit for colligative properties (because then the solution properties do not depend on the identity of the solute). Therefore, we can shift from molarity concentration units to molality concentration units].

For dilute solutions (< 0.001m), the electrostatic attractions can be neglected, so

$$a_i = m_i$$

and value of γ_i becomes unity. For an electrolyte, such as NaCl, the activity of Na^+ and Cl^- ions can be written as

$$a_+ = \gamma_+ m_+$$

and $$a_- = \gamma_- m_-$$

Since it is not possible to get only positive or negative ions in the solution of an electrolyte, there is no experimental method available to determine the activity or activity coefficient of individual ionic species. The reasons is that the solutions are electrically neutral and we cannot increase the number of cations without an equal increase in the number of anions. Since we cannot study separately the effect of cations or anions in the presence of each other in a neutral solution, it is therefore, not possible to measure the individual ion activities. Fortunately for most purposes, it is sufficient to know the mean ionic activity ($a_\pm$) and mean activity coefficient ($\gamma_\pm$).

Since it is not possible to substitute concentrations for activities in ionic solutions, it is essential to consider how the ionic concentrations may be converted to the activities and how such activities can be evaluated. In order to introduce some definitions commonly employed in dealing with the activities of strong electrolytes. Consider an electrolyte A_xB_y which ionizes in the solution according to

$$A_xB_y = xA^{z+} + yB^{z-}$$

When Z+ and Z- are the charges on the cation and anion respectively. The activity of the electrolyte as a whole, a_2, is defined in terms of the activities of the two ions, a_+ and a_- as

$$a_2 = a_+^x a_-^y \tag{9.64}$$

If V is the total number of the ions furnished by one molecule of the electrolyte, i.e., V = x + y, then mean activity is defined as

$$a_\pm = (a_2)^{1/v} = (a_+^x a_-^y)^{1/v} \tag{9.65}$$

The activities of the ions are related to their concentrations through the relation.

$$a_+ = \gamma_+ m_+ \tag{9.66}$$

$$a_- = \gamma_- m_- \tag{9.67}$$

Where m_+ and m_- are the molalities of the cation and anions and γ_+ and γ_- are the corresponding activity coefficients. These activity coefficients are appropriate factors which when multiplied by the molalities of the respective ions yield their activities. Introducing Eq (9.66) and (9.67) into Eq (9.64), we obtain for a_2

$$a_2 = (m_+\gamma_+)^x \, (m_-\gamma_-)^y$$

$$a_2 = (m_+^x m_-^y)\ (\gamma_+^x \gamma_-^y) \qquad (9.68)$$

and for mean activity from Eq. (9.65)

$$a_\pm = (a_2)^{\frac{1}{v}} = (m_+^x m_-^y)^{\frac{1}{v}} \gamma_+^x \gamma_-^y)^{\frac{1}{v}} \qquad (9.69)$$

The factor $(m_+^x m_-^y)^{\frac{1}{v}}$ is defined as the mean molality of the electrolyte.

$$m_\pm = (m_+^x m_-^y)^{\frac{1}{v}}$$

Similarly $(\gamma_+^x \gamma_-^y)^{\frac{1}{v}}$ is known as mean activity coefficient

$$\gamma_\pm = (\gamma_+^x \gamma_-^y)^{\frac{1}{v}}$$

In terms of mean molality and mean activity coefficient. Eq (9.68) and (9.69) may be written as

$$a_2 = a_\pm^v = m_\pm \gamma_\pm \qquad (9.70)$$

$$a_\pm = a_2^{\frac{1}{v}} = (m_\pm \gamma_\pm)^v \qquad (9.71)$$

Finally since for any electrolyte of molality m. we have

$$m_+ = xm$$

$$m_- = ym$$

Eqs. (9.70) and (9.71) then take the form

$$a_\pm = (m_+^x m_-^y)^{\frac{1}{v}} \gamma_\pm$$

$$= \left[(xm)^x (ym)^y\right]^{\frac{1}{v}} \gamma_\pm$$

$$= \left[\left(x^x m^x\right)\left(y^y m^y\right)\right]^{\frac{1}{v}} \gamma_\pm$$

$$= \left[\left(x^x y^y\right)^{\frac{1}{v}} \left(m^{x+y}\right)\right]^{\frac{1}{v}} \gamma_\pm$$

$$= \left(x^x y^y\right)^{\frac{1}{v}} m\ \gamma_\pm \qquad (9.72)$$

and $$a_2 = (a_\pm)^v = \left[(x^x y^y)^{\frac{1}{v}} m\ \gamma_\pm\right]^v$$

$$= \left(x^x y^y\right) m^v \gamma_\pm^v \qquad (9.73)$$

Equation (9.72) and (9.73) are the expressions needed for converting activities to molalities, or vice versa. Thus for 1:1 electrolyte such as KCl, of molality m, we have x = 1, y = 1, V = 2 and therefore.

$$a_{\pm} = (1 \times 1)^{1/2} m\ \gamma_{\pm}$$

$$a_2 = a_{\pm}^2 = m^2 \gamma_{\pm}^2$$

Again for an electrolyte of the 2:1 type, such as $BaCl_2$, we have x = 1, y = 2 and V = 3.

$$a_{\pm} = \left(1 \times 2^2\right)^{1/3} m\ \gamma_{\pm}$$

$$= (4)^{1/3} m\ \gamma_{\pm}$$

$$a_2 = a_{\pm}^3 = 4m^3 \gamma_{\pm}^3$$

Example 9.5.

Calculate the mean and total activity of the following electrolytes: (i) $CuSO_4$ (ii) Na_3PO_4 (iii) $Ca_3(PO_4)_2$

Solution:

(i) $CuSO_4$ x = 1, y = 1. and V = 1 + 1 = 2

$$a_{\pm} = (1 \times 1)^{1/2} m\ \gamma_{\pm}$$

$$= m\gamma_{\pm}$$

$$a_2 = (a_{\pm})^2 = m^2 \gamma_{\pm}^2$$

(ii) Na_3PO_4 x = 3, y = 1, V = x + y = 4

$$a_{\pm} = (3^3 \times 1^1)^{1/4} m\ \gamma_{\pm} = (27)^{1/4} m\gamma_{\pm}$$

$$a_2 = (a_{\pm})^4 = 27 m^4 \gamma_{\pm}^4$$

(iii) $Ca_3(PO_4)_2$ x = 3, y = 2, V = x + y = 3 + 2 = 5

$$a_{\pm} = (3^3 2^2)^{1/5} m\ \gamma_{\pm} = (108)^{1/5} m\ \gamma_{\pm}$$

$$a_2 = 108 m^5 \gamma_{\pm}^5$$

Example 9.6. Calculate the mean activity of the ions and activity of the electrolyte in 0.1m NaCl solution. The $\gamma_{\pm}$ is 0.778.

Solution:

$$m = 0.1 \text{ and } \gamma_{\pm} = 0.778$$

$$a_{\pm} = m\gamma_{\pm} = 0.1 \times 0.778 = 0.0778$$

$$a_2 = (a_{\pm})^2 = (0.0778)^2 = 6.05 \times 10^{-3}$$

9.20 DEBYE- HUCKEL LIMITING LAW

One of the most significant contributions to our understanding of the behavior of electrolyte solutions is the Debye-Huckel limiting law. Debye and Huckel (1923) derived an equation which offers quantitative calculation of mean activity coefficients of strong electrolytes. The values obtained theoretically were in good agreement with the experimental values as long as the concentrations are kept low. The equation which they derived is known as Limiting Law equation. The name signifies that its application is limited to dilute solutions of strong electrolytes only. This limiting law is based on the following assumptions:

(i) Electrolytes are completely dissociated into ions in solution.

(ii) The solutions are dilute, with a concentration of 0.01m or lower.

(iii) The interactions between ions of solute are electrostatic in character. Electrostatic forces are strictly long rang interactions.

(iv) The ions in the solution are subject to random thermal motion which disrupts the orientation of oppositely charged species caused by the interionic attractions.

(v) Each ion is regarded as point charge and is surrounded by ions of opposite charge, forming an ionic atmosphere.

(vi) The dielectric constant of an electrolyte solution is uniform and independent of the actual concentration of the dissolved solute.

The energy associated with the ionic atmosphere is electrical in origin. It therefore, must be a function of charge density and the potential produced by the ionic atmosphere. According to Debye-Huckel theory the energy of ionic interaction is electrostatic in origin and may be defined as the energy of charging a central ion in the electric field of an ionic cloud.

The energy of a charged body, that is the work expended in the process of charging, is half the product of its charge and potential. Hence for an ion of charge $+Z_i \epsilon$ the energy it possesses by virtue of its ionic atmosphere is given as

$$E_i = \frac{1}{2}\,(\text{charge})\,(\text{potential})$$

$$E_i = \frac{1}{2}\,(Z_i \epsilon)\left(\frac{-Z_i \epsilon k}{D}\right)$$

$$E_i = -\frac{Z_i^2 \epsilon^2 k}{2D}$$

The corresponding energy for a 1 g ion is obtained on multiplying by the Avogadro number, N, so that

$$E_i = -\frac{NZ_i^2 \epsilon^2 K}{2D} \qquad (9.74)$$

According to the definition of chemical potential the chemical potential of a particular ion in an ideal solution is given by

$$\mu_i = \mu_i^o + RT\ln x_i \qquad (9.75)$$

When x_i is mole fraction in the given solution. For a non-ideal solution one can write

$$\mu_i = \mu_i^o + RT\ln a_i$$

$$\mu_i = \mu_i^o + RT\ \text{in}\ a\ x_i + RT\ \ln \gamma_i \qquad (\therefore a_i = \gamma_i x_i) \qquad (9.76)$$

Where a_i is the activity and γ_i the activity coefficient of ionic species. The difference between Eqs (9.75) and (9.76) is $RT\ln\gamma_i$ which is equal to the difference in free energy change accompanying the addition or removal of 1g ion of the given species from a large volume of real and ideal solution respectively. This difference of free energy may be regarded as, equivalent to the electrical energy of the ion due to its atmosphere; that is to say, the departure from ideal behavior is ascribed entirely to interionic forces. Hence Eq. (9.74) became as.

$$RT\ln\gamma_i = -\frac{NZ_i^2 \in^2 k}{2D}$$

$$\ln\gamma_i = -\frac{NZ_i^2 \in^2 k}{2DRT} \qquad (9.77)$$

From Eq. (9.38), we know

$$k = \left(\frac{4\pi \in^2 \sum n_i Z_i^2}{DkT}\right)^{1/2}$$

or $$k = \frac{2\in(\pi)^{1/2}(\sum n_i Z_i^2)^{1/2}}{(DkT)^{1/2}}$$

Where n_i is the number of ions per ml. It may be replaced by $NC_i/1000$, where C_i is the number of gram ions dissolved per liter, k is the Boltzmann constant, $k = R/N$

$$k = \frac{2\in(\pi)^{1/2}\left(\sum \frac{NC_i}{1000} Z_i^2\right)^{1/2}}{\left(\frac{DRT}{N}\right)^{1/2}}$$

$$k = \frac{2\in\left(\frac{\pi}{1000}\right)^{1/2}(N)^{1/2}\left(\sum C_i Z_i^2\right)^{1/2}}{\left(\frac{DRT}{N}\right)^{1/2}}$$

$$k = \frac{2\epsilon\left(\frac{\pi}{1000}\right)^{1/2} N\left(\sum C_i Z_i^2\right)^{1/2}}{(DRT)^{1/2}} \qquad (9.68)$$

Substituting this value of K into Eq. (9.77), we get

$$\ln \gamma_i = \frac{-NZ_i^2 \epsilon^2}{2\ DRT} \cdot \frac{2\epsilon\left(\frac{\pi}{1000}\right)^{1/2} N\left(\sum C_i Z_i^2\right)^{1/2}}{(DRT)^{1/2}}$$

Multiplying both sides by negative and on rearranging we get

$$-\ln \gamma_i = \frac{N^2 Z_i^2 \epsilon^3}{DRT} \cdot \frac{\left(\frac{\pi}{1000}\right)^{1/2}\left(\sum C_i Z_i^2\right)^{1/2}}{(DRT)^{1/2}}$$

$$-\log \gamma_i = \frac{N^2 \epsilon^3 \left(\frac{\pi}{1000}\right)^{1/2}}{2.303\ R^{3/2}} \cdot \frac{Zi^2\left(\sum C_i Z_i^2\right)^{1/2}}{(DT)^{3/2}} \qquad (9.79)$$

The term in the large parentheses consists of several constants, only and may be replaced by A′.

$$-\log \gamma_i = \frac{A' Z_i^2 \sqrt{\sum C_i Z_i^2}}{(DT)^{3/2}} \qquad (9.80)$$

Further, we know that

$$\mu = \frac{1}{2} \sum C_i Z_i^2$$

$$2\mu = \sum C_i Z_i^2 \qquad (9.81)$$

Substituting the value of $\sum C_i Z_i^2$ from Eq. (9.81) into Eq. (9.80) we get

$$-\log \gamma_i = \frac{A' Z_i^2 \sqrt{2\mu}}{(DT)^{3/2}}$$

$$-\log \gamma_i = \frac{A' \sqrt{2}\, Z_i^2 \sqrt{\mu}}{(DT)^{3/2}}$$

$$-\log \gamma_i = \frac{A'' Z_i^2 \sqrt{\mu}}{(DT)^{3/2}} \qquad (9.82)$$

For a given solvent and temperature, D and T have definite values which may be inserted into Eq. (9.82) to give

$$\log \gamma_i = -A\ Z_i^2 \sqrt{\mu} \tag{9.83}$$

By inserting the values of N, E, π, R, D, and T, the value of A is found to be 0.509 at 25°C, hance

$$-\log \gamma_i = 0.509\ Z_i^2 \sqrt{\mu} \tag{9.84}$$

Eqs. (9.83) and (9.84) represent the Debye-Huckal limiting law. This expresses the variation of the activity coefficient of an ion with the ionic strength of the solution. It is expected to hold for dilute solutions of electrolytes as is clear from the fact that the expression for the potential of an ion due to ionic atmosphere was derived assuming dilution being approached. Moreover, from Eq (9.84). It follows that activity coefficient of an ion should decrease with increasing ionic strength of the solution.

Since the individual activity or activity coefficient, of an ion cannot be determined experimentally, it is not possible to make direct test of Eq. (9.83) However, it is possible to relate the individual ion activities to the measurable mean activities of the ions. If one molecule of a binary electrolyte dissociates into V ions of which V+ are cations and V- anions, then the mean activity coefficient is related to individual ionic activity coefficient γ_+ and γ_- by

$$\gamma_{\pm} = (\gamma_+^{v+}\ \gamma_-^{v-})^{1/v}$$

$$\log \gamma_{\pm} = \frac{1}{v} \log\,(\gamma_+^{v+}\ \gamma_-^{v-})$$

$$= \frac{1}{v}\left[\log \gamma_+^{v+} + \log \gamma_-^{v-}\right]$$

$$= \frac{1}{v}\left[V_+ \log \gamma_+ + V_- \log \gamma_-\right] \tag{9.58}$$

If the valences of the ions are Z+ and Z- respectively, then by the relationship between the value and the number of ions, i.e., $V_+Z_+ = V\_Z\_$, it follows that

$$\frac{V_+}{V_-} = \frac{Z_-}{Z_+}$$

$$\log \gamma_{\pm} = \frac{1}{v_+ + v_-}\left[Z_- \log \gamma_+ + Z_+ \log \gamma_-\right]$$

$$\log \gamma_{\pm} = \frac{1}{v_+ + v_-}\left[Z_-\left(-AZ_+^2\sqrt{\mu}\right) + Z_+(-AZ_-^2\sqrt{\mu}\right]$$

$$\log \gamma_{\pm} = -\frac{A\,Z_+Z_-\sqrt{\mu}\ (Z_+ + Z_-)}{Z_- + Z_+}$$

$$\log \gamma_\pm = -A\, Z_+ Z_- \sqrt{\mu} \tag{9.86}$$

Equation (9.86) also represents the Debye-Huckal limiting law for dilute solutions. According to this law the deviation from the ideal behavior in a given solvent is governed by the ionic strength of the medium and valence of the ions of electrolyte, but is independent of their chemical nature.

Verification of the Debye-Huckel Limiting Law:

The mean activity coefficients of various electrolytes can be determined experimentally by a number of methods, e.g. measurement of vapour pressure, freezing point, solubility or electromotive force. In general, it is found that the mean activity coefficient of an electrolyte decreases with increasing concentration, but at higher concentration range it is frequently found that the mean activity coefficient increases with increasing concentration. thus passing though a minimum.

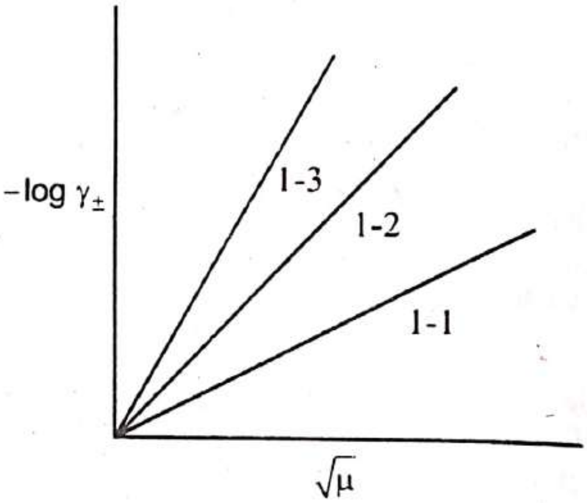


Fig. 9.7. Test of Debye-Huckel limiting law for diffent electrolytes.

The law can be tested by plotting a graph between $-\log \gamma_\pm$ and $\sqrt{\mu}$, at room temperature. All electrolytes should give a straight line passing through the origin. The slope of the line depends on Z_+ and Z_- values of the given electrolytes. For electrolytes this slope should be A, for 1-2 or 2-1 type electrolytes 2A for 1-3 or 3-1 electrolytes 3A etc.

Example 9.7. Calculate the mean activity coefficient of (i) a 1-1 electrolyte, e.g., NaCl at a molility of 0.01 and of (ii) 1-2 electrolyte, e.g., Na_2SO_4 at a molality of 0.001 in aqueous solution of 25°C.

Solution:

(i) For 1-1 electrolyte, the ionic strength is equal to its molality, hence $\mu = 0.01$, $Z_+ = Z_- = 1$, so

$$\log \gamma_\pm = -0.509 \times 1 \times 1\sqrt{0.01}$$

$$\log \gamma_\pm = -0.0509$$

$$\gamma_\pm = -0.889$$

(ii) For 0.001 molal 1-2 electrolyte.

$$\mu = \frac{1}{2}(0.002 \times 1^2 + 0.001 \times 2^2)$$

$$\mu = 0.003$$

$$\log \gamma_\pm = -0.509 \times 1 \times 2\sqrt{0.003}$$

$$\log \gamma_\pm = -0.0558$$

$$\gamma_\pm = 0.879$$

9.21. DETERMINATION OF ACTIVITY COEFFICIENTS OF ELECTROLYTES

The mean activity coefficients of various electrolyte can be determined experimentally by a number of methods. Some of them are:

(i) Solubility method

(ii) Vapour pressure method

(iii) Freezing point method

(iv) Electromotive force method

(v) Equilibrium constant method.

It is important to note that activity coefficient of a single ion cannot be determined experimentally, because it is impossible to isolate an ion in free state. Hence only mean activity coefficients of various electrolytes, are usually determined. We shall discuss here some of these methods.

(i) Solubility Method:

This method is particularly used for sparingly soluble salts. When a solution is saturated with a salt there is an equilibrium between the excess solid and the ions in the solution. To consider a simple case, such as that of sparingly soluble salt silver chloride in contact with its saturated solution, the equilibrium may be represented by

$$AgCl_{(s)} \rightleftharpoons Ag^+ + Cl^-$$

Where Ag^+ and Cl^- ions refer to the hydrated ions in the solution. The corresponding equilibrium constant is given as

$$K = \frac{a_{Ag^+} \times a_{Cl^-}}{a_{AgCl}} \qquad (9.87)$$

Since the silver chloride is present in the solid state, its activity is taken as unity by convention.

$$K.(a_{AgCl}) = (a_{Ag^+})(a_{Cl^-}) \qquad \therefore a_{AgCl} = 1$$

$$K_S = (a_{Ag^+})(a_{Cl^-}) \qquad (9.88)$$

Where the constant, K_S is known the solubility product constant of the silver chloride.

In general for any electrolyte having the general formula AB(s), in contact with its saturated solution, the equilibrium between the solid and the ions in solution is

$$AB_{(s)} \rightleftharpoons A^+ + B^-$$

and the solubility product constant is given by

$$K_s = (a_{A^+})(a_{B^-}) \tag{9.89}$$

This expression is the basis of the solubility product principle which states that when a solution is saturated with a given salt, the product of the activities (or concentrations) of its constituent ion, raised to the appropriate powers, must be constant, irrespective of the nature of other electrolytes present in the solution.

If the activity of each ion is written as the product of its concentration in gram ions per liter and the corresponding activity coefficient, then the expression for the solubility product of $AB_{(s)}$ becomes.

$$K_s = \gamma_+[A^+]\,\gamma_-[B^-]$$

$$K_s = \gamma_+\gamma_-[A^+][B^-]$$

$$K_s = \gamma_\pm^2[A^+][B^-]$$

Taking logarithms on both sides we get (on rearranging)

$$\log K_s = \log \gamma_\pm^2 + \log [A^+][B^-]$$

$$\log K_s = 2\log \gamma_\pm + \log [A^+][B^-]$$

$$\log [A^+][B^-] = \log K_S - 2\log \gamma_\pm$$

The solubility 'S' of such a salt is equal to the moles per liter of the salt that dissolves, if no species of electrolyte $AB_{(S)}$ other than A^+ and B^- exist in solution.

$$[A^+] = [B^-] = S$$

Thus $\log S.S. = \log K_S - 2\log \gamma_\pm$

$$\log S^2 = \log K_S - 2\log \gamma_\pm$$

$$2\log S = \log K_S - 2\log \gamma_\pm$$

$$\log S = \frac{1}{2}\log K_S - \log \gamma_\pm \tag{9.90}$$

Since K_s is solubility product, and is constant at a given temperature, so variation of mean activity coefficient i.e, $\gamma_\pm$, can be related with the solubility of that compound at a given temperature. In order to find the utility of last equation, now consider the data that are obtained when a sparingly soluble salt is dissolved in solutions that contain various amounts of neutral or non-reacting electrolyte, that do not contain the ions A^+ or B^- Debye-Huckel theory again suggests that at low ionic strength.

$$-\log \gamma_{\pm} = 0.5091\, Z_i^2 \sqrt{\mu}$$

$$-\log \gamma_{\pm} \propto \sqrt{\mu}$$

Hence we write the previous equation.

$$\boxed{\log S = \frac{1}{2}\log K_S + 0.5091\, Z_i^2 \sqrt{\mu}} \qquad (9.91)$$

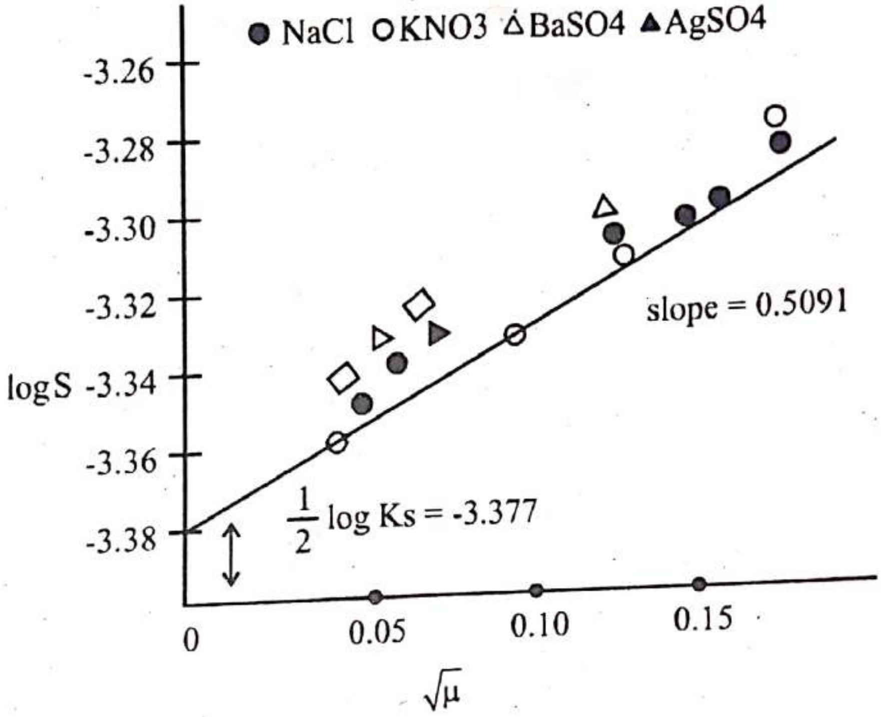


Fig. 9.8 Calculation of K_s by extra-polation method

If "log S" is plotted against $\sqrt{\mu}$ by using a complicated but experimentally convenient salt $[Co(NH_3)_4C_2O_4][Co(NH_3)_2(NO_2)_2C_2O_4]$, a straight line is obtained, which supports Deby-Huckel predictions of linear relation and straight line has been drawn with predicted slope of 0.5091

The Fig 9.8 shows the effect of added salts on the solubility of a salt $[Co(NH_3)_4C_2O_4][Co(NH_3)_2(NO_2)_2C_2O_4]$ containing a singly charged cation and a singly charged anion. For this particular set of data that the linear relation is rather rough and that support for Debye-Huckel theory is given but is not very convincing here. It is just such difficulties that the theory frequently encounters particularly in solutions other than those of extremely low ionic strength.

An extrapolation can be made in Fig 9.8 with/ without D.H.T and one obtains for the L.H.S of equation (9.91) at zero ionic strength, the value –3.377. Again the limit of zero ionic strength corresponds to the complete absence of ionic interactions. Therefore.

$$\gamma_{\pm} = 1 \qquad \text{and} \qquad \log \gamma_{\pm} = 0$$

At this limit equation 9.91 gives

$$\frac{1}{2}\log K_s = -3.377$$

$$\log K_s = -6.754$$

$$K_s = \text{Antilog}(-6.754)$$

$$K_s = 1.76 \times 10^{-7}$$

With this value one is again able to learn equation 9.91 around to give an expression for the activity coefficient of the singly soluble salt at any concentration.

$$\boxed{\log \gamma_{\pm} = -3.377 - \log S} \tag{9.92}$$

The solubility data, used to construct Fig-(9.8) can therefore be made to give $\gamma_{\pm}$ for the dissolved salt in all the solutions studied. Although, the D.H.T.was used to aid in the extrapolation to obtain "K_s" in Fig 9.8, it should be recognized that these results do not depend on this theory and are valid for any aqueous solution at this temperature, for which the solubility of the salt can be measured.

(ii) Activity Coefficients from the Dissociation of a weak electrolyte

Other studies of chemical equilibria besides those that make use of oxidation-reduction reactions in electrochemical cells, can be used to deduce thermodynamic properties of non-ideal systems. Acid-base equilibria provide many illustrations. The traditional example is the equilibrium set up by the dissociation of acetic acid, CH_3COOH, here abbreviated HAc.

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

or $$HAc \rightleftharpoons H^+ + Ac^-$$

The thermodynamic equilibrium constant, denoted by K_{th} is given

$$K_{th} = \frac{(a_{H^+})(a_{AC^-})}{(a_{HAc})}$$

$$K_{th} = \frac{\gamma_+\gamma_-[H^+][Ac^-]}{\gamma_{HAc}[HAc]} \tag{9.93}$$

This expression is simplified when it is realized that the electrostatic interactions are primarily responsible for the non-ideality which produces activity coefficient different from unity. The uncharged HAc molecule should therefore behave relatively ideally, and we can set $\gamma_{HAc} = 1$

$$K_{th} = \frac{\gamma_{\pm}^2[H^+][Ac^-]}{[HAc]} \tag{9.94}$$

Taking log of the above expression and on rearranging we get

$$\log K_{th} = \log \left[\frac{\gamma_\pm^2 [H^+][Ac^-]}{[HAc]} \right]$$

$$\log K_{th} = \log \gamma_\pm^2 + \log \frac{[H^+][Ac^-]}{[HAc]}$$

$$\log K_{th} = 2 \log \gamma_\pm + \log \frac{[H^+][Ac^-]}{[HAc]}$$

$$\log \frac{[H^+][Ac^-]}{[HAc]} = \log K_{th} - 2 \log \gamma_\pm \tag{9.95}$$

Since HAc is partially dissociated, so the concentration of dissociated and un-dissociated acetic acid may be substituted in the above expression by considering the degree of dissociation $(\propto)$. Let

$$HAc \rightleftharpoons H^+ + Ac^-$$

1 mole $\quad 0 + 0 \quad t = 0$

$(1-\alpha)$ mole $\quad \alpha + \alpha \quad$ after t – sec

Where α =no of moles converted to ions and it is also known as degree of dissociation. Let the concentration of CH_3COOH is taken as "C" moles liter. Then at equilibrium stage.

$$C(1-\alpha) \rightleftharpoons C\alpha + C\alpha$$

Substitute then values of concentration in Eq. (9.95) we get

$$\log \frac{C\alpha . C\alpha}{C(1-\alpha)} = \log K_{th} - 2 \log \gamma_\pm$$

$$\log \frac{C\alpha^2}{(1-\alpha)} = \log K_{th} - 2 \log \gamma_\pm \tag{9.96}$$

For solutions that are very dilute in ions one can still use the Arrhenius expression to obtain the degree of dissociation from the conductivity measurement.

$$\alpha = \frac{\Lambda}{\Lambda_0} = \frac{\text{equivalent conductance at given cancentration}}{\text{equivalent conductance at infinite dilution}}$$

In this way, the left side of Eq. (9.96) is determined for various acetic acid concentrations. The right side consists of a constant term log K_{th} and a term which the D.H. theory suggests will, at low concentrations, be proportional to the square root of the ionic strength.

$$-\log \gamma_\pm \propto \sqrt{\mu}$$

If the solution contains only the H^+ and Ac^- ions from the dissociation of HAc, one has

$$\mu = \frac{1}{2}\left[(C\alpha)(1)^2 + (C\alpha)(-1)^2\right]$$

$$\mu = C\alpha$$

and $$\sqrt{\mu} = \sqrt{C\alpha}$$

so $$\log \frac{C\alpha^2}{1-\alpha} = \log K_{th} + 2(0.5091\, Z_+Z_-\sqrt{\mu})$$

$$\log \frac{C\alpha^2}{1-\alpha} = \log K_{th} + 1.018\, Z_+Z_-\sqrt{C\alpha} \qquad (9.97)$$

Equation (9.97) is an equation of straight-line,

$$\log \frac{C\alpha^2}{1-\alpha} = \log K_{th} + 1.018\sqrt{C\alpha}$$ $\therefore$ electrolyte is 1:1 type $Z_+ = Z_- = 1$

If a graph is plotted between $\log \frac{C\alpha^2}{1-\alpha}$ v/s $\sqrt{C\alpha}$ a straight-line is obtained with slope 1.018 and intercept log K_{th}.

Extrapolation to zero ionic strength, when $\gamma_\pm = 1$ and $\log \gamma_\pm = 0$, gives

$$\log K_{th} = -4.7565$$

and $$K_{th} = \text{antilog}(-4.7565)$$

$$K_{th} = 1.752 \times 10^{-5}$$

$$K_{th} = 1.752 \times 10^{-5}$$ (theoretical)

$$K_{th} = 1.8 \times 10^{-5}$$ (experimental)

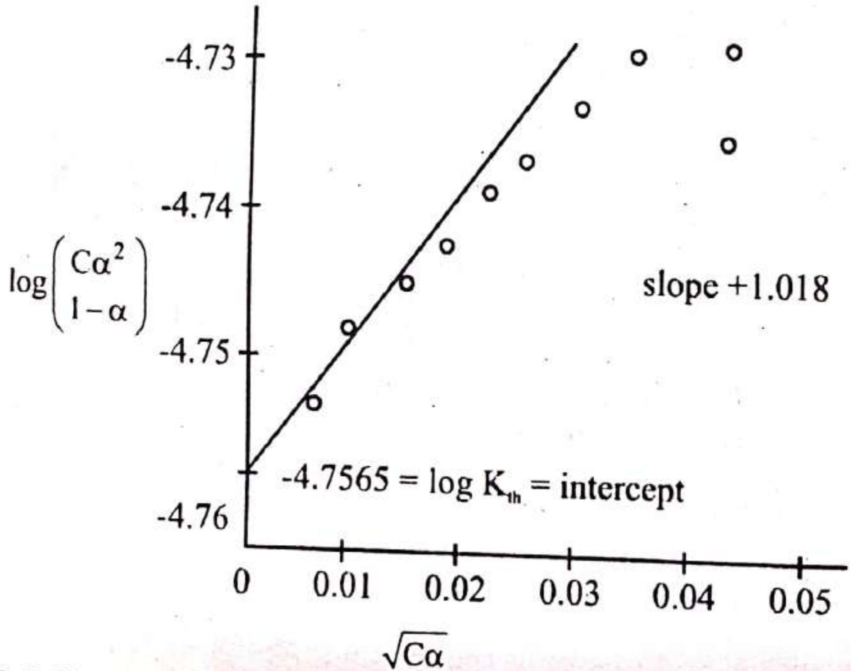


Fig. 9.9. Representation of experimental data for weak electrolyte

The value of K_{th} is very close to experimental value, so D.H.L can be used to calculate the thermodynamic equilibrium constant of weak electrolyte.

Equation (9.96) can also be now rearranged to give.

$$\log \gamma_{\pm} = \frac{1}{2} \log K_{th} - \frac{1}{2} \log \frac{C\alpha^2}{1-\alpha}$$

$$\log \gamma_{\pm} = -2.3782 - \frac{1}{2} \log \frac{C\alpha^2}{1-\alpha} \tag{9.98}$$

From equation (9.98), we can determine $\gamma_{\pm}$ for the dissociation products of CH_3COOH at any concentrations for which values of α can be obtained.

QUESTIONS

Q.1. (a) Define electrochemistry. Discuss the significance of electrochemistry in daily life.

(b) Explain how does the metallic conduction differ from electrolytic conduction.

(c) Why the electrolytic conduction increases with rise in temperature while metallic conduction decreases.

Q.2. (a) Define Ohm's law. Explain the various terms involved.

(b) Define and explain the terms conductance, specific conductance and specific resistance.

(c) Compare equivalent conductance with molar conductance.

Q.3. (a) What is cell constant? How is it determined?

(b) Explain the significance of cell constant.

(c) 0.01M solution of KCl has a specific conductance of 0.00001413 Sm^{-1} at 25°C. Its measured resistance in a conductivity cell was 94.3 ohm. When the cell was fitted with 0.02 M $AgNO_3$ solution, its resistance was found to be 50.3 ohm. Calculate the specific conductance of $AgNO_3$ solution.

$(Ls = 2.64 \times 10^{-5} Sm^{-1})$

Q.4. (a) When a conductance cell was filled with 0.02 M solution of KCl, which had a specific conductance of 0.2767 Sm^{-1}; it had a resistance of 82.39 ohm at room temperature. When the same cell was filled with 2.5×10^{-3} M solution of K_2SO_4 its resistance was 325 ohm. Calculate the cell constant and specific conductance of K_2SO_4 solution.

(Cell constant = $22.80 m^{-1}$, $Ls = 7.01 \times 10^{-2} Sm^{-1}$)

Q.5. (a) How is the conductance of an electrolyte measured? Explain the Wheat stone bridge circuit with suitable diagram.

(b) Explain why the specific conductance decreases on dilution while molar conductance increases.

(c) Explain the variation of equivalent conductance of strong and weak electrolytes with dilution.

Q.6. (a) Discuss the effect of temperature, dieelectric constant and viscosity of the medium on the conductance of an electrolyte.

(b) What is Arrhenius theory of electrolytic dissociation? Explain its various postulates.

(c) Why Arrhenius theory is not applicable to strong electrolytes?

Q.7. (a) Define and explain Ostwald's dilution law.

(b) How is the law verified experimentally.

Q.8. (a) Explain the effect of concentration on equivalent conductance of weak electrolytes.

(b) Discuss the effect of concentration on equivalent conductance of strong electrolytes.

Q.9. Why the equivalent conductance increases as dilution in case of strong electrolytes? Discuss Debye-Huckel theory of interionic attraction.

Q.10. (a) Explain Debye-Huckel theory of strong electrolytes.

(b) Derive the expression for ionic atmosphere around a central ion.

Q.11. (a) Drive Debye-Huckel-Onsager conductance equation.

(b) Discuss the validity and deviation from D.H.O. equation.

Q.12. (a) Define ionic strength of a solution. Explain its significance in electrochemistry.

(b) Calculate the ionic strength of a solution that is 0.30m in KNO_3 and 0.1m in $CaCl_2$.

Q.13. (a) What is Debye-Huckel Limiting law? Prove the following equation.

$$-\log \gamma_{\pm} = A\, Z_{+} Z_{-} \sqrt{\mu}$$

(b) Why Debye-Huckel law is valid for dilute solutions only?

(c) How would you test the validity of Debye-Huckel law?

(d) Calculate the mean activity coefficient of 0.1m NaCl solution.

Q.14. (a) What is the difference between activity and concentration?

(b) Explain the significance of activity coefficient.

(c) Derive the expressions for total and mean activity of strong electrolytes.

Q.15. (a) What do you mean by mean activity coefficient.

(b) How would you determine mean activity coefficient by solubility method.

(c) Explain the measurement of men activity coefficient from the dissociation of weak electrolytes.

Q.16. Justify or comment on the following statements.

(i) Metals are good conductor of electricity.

(ii) Metallic conductors are also known an ionic conductors.

(iii) Ionic conduction decreases with rise in temperature.

(iv) The units of conductance is ohm.

(v) The unit of specific conductance is Sm^{-1}.

(vi) The dimensions of cell constant is m^{-1}.

(vii) Specific conductance decreases with increase in concentration.

(viii)Equivalent conductance increases on dilution.

(ix) Direct current is not used in conductance measurement.

(x) Asymmetric effect is also known as relaxation affect.

(xi) Ionic strength of 1:1 electrolyte is equal to its molarity.

(xii) Individual ion activities cannot be determined.

(xiii)Interionic attractions are responsible for deviation from ideal behavior in case of strong electrolytes.

(xiv)Debye-Huckel law is valid to dilution solution only.

(xv) A positive ion has an ionic atmosphere of negative ion.

REFERENCES

1. Glasstone, S. 1995. Physical Chemistry, Macmillan and Co. Ltd. St. Marlins Street, London.
2. Maron, S. H. and C. F. Prutton, 2000. Principles of Physical Chemistry, 4th Edition, The Macmillan Company collier-Macmillan Limited, London.
3. Kundu S. and S.K. Jain. Physical Chemistry, S. Chand and Co (Pvt) Ltd,.India.
4. Atkins, P.W. 2005. Physical Chemistry, Freeman and Company, New York.
5. Silbey, R. J. Alberty, R. A. and M. G. Bawendi 2005. Physical chemistry, Wiley, India.
6. Barrow, G.M. 1995. Introduction to Molecular Spectroscopy, McGraw-Hill, New York.
7. Fried, V.B. and H.F Hameka. 2004. Physical Chemistry, Macmillan Publishing Company, New York.
8. Laidler, K.J. and J.H. Meiser. 2000. Physical Chemistry, Longman publishers New Delhi India.
9. Glasstone, S. 1997. An Introduction to Electrochemistry, Affiliated East-West press pvt. Limite New Delhi.
10. Gastellan, G.W. 2001. Physical Chemistry. Narosa Publishing House, New, Delhi.
11. Ball, D.W. 2000. Physical Chemistry, Thomson books/ U.K.
12. Simon J.D. and D.A. McQuarrie. 2001. Physical Chemistry, Viva Book Private limited New Delhi.

Chapter 10

ELECTROCHEMICAL CELLS

10.1 INTRODUCTION

Electrochemical cells are defined as systems consisting of two metallic electrodes, dipping into the same or different electrolytes, in electrical communication. These cells may be used to perform two functions namely, (i) to convert chemical energy into electrical energy and (ii) convert electrical energy into chemical energy. Electro chemical cells can be broadly classified into two categories, viz, electrolytic cells and galvanic (or voltaic) cells. In the former, a chemical reaction is carried out with the help of electrical energy (electric current), whereas in the latter an electric current is produced as a result of some spontaneous chemical reaction. Thus, an electrolytic cell is a device to convert electrical energy into chemical energy whereas in the galvanic cell, the reverse of the process take place.

Electrochemical reactions involve electrons that are transferred from a metal to a species in a solution. The equilibriam of electro chemical reactions are important in galvanic cells and electrolytic cells. The measurement of electromotive force of an electrochemical cell over a range of temperature makes it possible to obtain the thermodynamic quantities for the reaction that occurs in the cell. The activity coefficients of electrolytes may also be calculated from there measurements.

Electrochemical cells are of practical interest in that they offer the means to convert the Gibbs free energy change of a chemical reaction to work. An understanding of the conversion of chemical energy to electrical energy is important for work with batteries fuel cells, electroplating, corrosion, electro-refining (e.g. production of aluminum) and electroanalytical techniques. Before proceeding a distinction should be made between the terms *cell* and *battery*. A cell is a single arrangement of two electrodes and an electrolyte of yielding electrical energy due to chemical reaction within the cell or of producing chemical reaction due to passage of electricity through the cell. e.g., common dry cell. A battery, on the other hard, is a combination of two or more cells arranged in series or parallel. Thus the ordinary 6-volt lead storage battery is a combination of three 2-volt cells connected in series

10.2 TYPES OF ELECTROCHEMICAL CELLS

Electrochemical cells are of two types: (i) Electrolytic cells and (ii) Galvanic or Voltaic cells. We will discuss each type briefly.

(i) Electrolytic cells: These are the cells in which electrical energy is consumed to bring about a chemical change. Hence in such cells energy consuming electrochemical change take place, e.g, electrolysis of aqueous solution of HCl into hydrogen and chlorine gases.

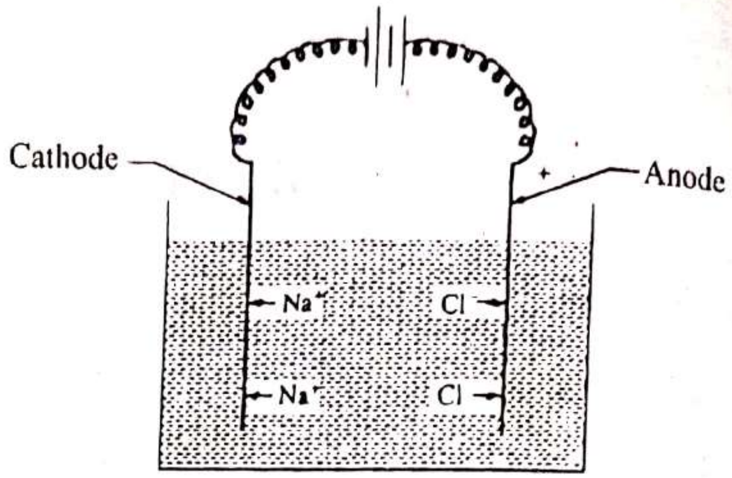


Fig. 10.1. Electrolytic cell

Consider an electrolytic cell involving the electrolysis of molten sodium chloride using platinum electrodes as shown in Fig-10.1. The left electrode is connected to the negative terminal of an external battery which supplies electrons to this electrode. It is because of this the left-side electrode becomes negativity charged. Electrons are being sucked but of the right-side electrode by the positive terminal of the battery and thus, this electrode acquires a positive charge. Within the solution, electricity is carried out by the movement of the ions. The positive ions (i.e., cations) are attracted towards the negative electrode and the negative ions (i.e., anions) towards the positive electrode. Since cations are attracted towards the negative electrode, the latter is known as the cathode. Similarly the positive electrode is known as the anode. Electrode reactions involve reduction at the cathode and oxidation at the anode. Thus in the present case, we have

$$\text{At cathode } Na^+_{(l)} + \bar{e} \longrightarrow Na_{(s)}$$

$$\text{At anode } Cl^-_{(l)} \longrightarrow \frac{1}{2}Cl_2(g) + \bar{e}$$

The overall transformation is

$$Na^+_{(l)} + Cl^-_{(l)} \longrightarrow Na_{(s)} + \frac{1}{2}Cl_{2(s)}$$

(ii) Galvanic cells: These are the cells in which the electrical energy is produced by the virtue of any physical or chemical process within the cell. The decrease in the free energy which provides a driving force in a galvanic cell may be due to a chemical reaction or any physical change occurring within the cell. The resulting cell is (a) *chemical or formation cell*, if the e.m.f. is due to a net chemical reaction occurring within the cell, and (b) *a concentration cell*, if the e.m.f is due to a process involving a transfer of matter from one part of the cell to the other one. Further, depending upon whether there exists an actual contact of the two solutions or not, the cells are classified as *cells with or without transfarence.*

A typical example of a galvanic cell is that of a *Daniell cell* (Fig. 10.2). In this cell a zinc electrode is dipped into a solution containing Zn^{2+} ions and a copper electrode immersed in a solution of Cu^{2+} ions. The two solutions are separated by a porous plug which allows electrical contact but prevents intermixing of electrolytes. The two half cells constitute the cell which is represented as

$$Zn \,|\, ZnSO_{4(aq)} \,\|\, CuSO_{4(aq)} \,|\, Cu$$

The single vertical line denotes the phase bounding and double vertical lines indicate that the liquid junction potential has been eliminated. Following reactions take place in the Daniell cell

$$Zn_{(s)} + CuSO_{4(aq)} \longrightarrow Cu_{(s)} + ZnSO_{4(aq)}$$

or in the ionic form

$$Zn_{(s)} + Cu^{2+}_{(aq)} \longrightarrow Cu_{(s)} + Zn^{2+}_{(aq)}$$

This reaction occurs at a very fast speed, i.e., the moment zinc is added to copper sulphate solution, copper is immediately formed. In this reactions, we have basically the following two partial reactions.

$$Zn_{(s)} \longrightarrow Zn^{2+} + 2\bar{e} \qquad \text{(oxidation)}$$

and $$Cu^{2+}_{(aq)} + 2\bar{e} \longrightarrow Cu_{(s)} \qquad \text{(reduction)}$$

If the two partial reactions are carried out in two physically separate places, the electrons will have to flow from a place where oxidation occurs to a place where reduction occurs through an external wire. This flow of electrons constitutes a current, which can be used to drive a motor, lift a mass, or to do any other work.

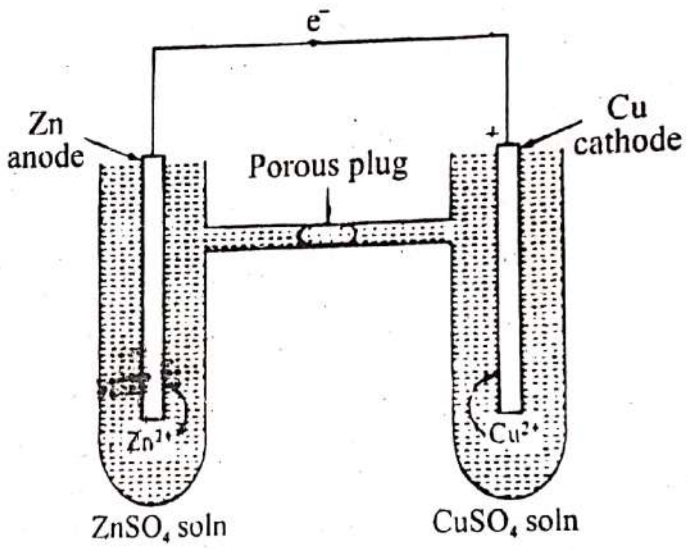


Fig 10.2. Daniell cell

The most obvious way to separate the partial reactions occurring in the Daniell cell is to insert Zn electrode into a solution containing Zn^{2+} ion (but not Cu^{21} ions) and the copper electrode (or some reactive metal) into a solution containg Cu^{2+} ions. From Zn electrode, a minute amount of Zn can go into the solution as Zn^{2+} ions leaving behind a negative charge on the electrode (because of electrons left behind) and a positive charge in the solution. These charges stop ionization process of zinc almost immediately; for every Zn^{2+} ion entering the solution, it or another ion will be driven back to the zinc electrode by the attraction of negative electrode and the repulsion of the positive solution. Similarly on the Cu electrode, a few Cu^{2+} ions from the solution may be deposited as Cu atoms. The process will make the electrode positive and solution negative and thus the deposition process is stopped. However, these processes at the two electrodes, namely oxidation at the Zn electrode and reduction at the Cu electrode can be resumed provided we connect the two electrodes by a wire to allow the electrons to flow from Zn electrode to the electron-deficient Cu electrode and bring the two solution into contact through a porous plug or a salt bridge, so as to neutralize the charges of the two solution and prevent a direct flow of Cu^{2+} ions towards Zn electrode.

10.3. ELECTRODE REACTIONS AND CONCEPT OF HALF-CELL

When two electrodes of a galvanic cell are connected by a conducting wire, certain chemical reactions take place within the cell. such reactions which involve the transfer of electrons from or to the electrode, are termed *electrode reactions*. These reactions are such that at one electrode the electrode material goes into the solution as positive ions, leaving the electrode with a net negative charge (or as negative ions, leaving a net positive charge on the electrode). The excess electrons are continuously sucked up by the other electrode. This flow of electrons then results into oxidation at one electrode (called anode), and reduction on the other, (called *cathode*). Thus each combination of electrode and the solution, in which it is immersed, called *half-cells*, behaves as an independent source of energy.

10.4. REVERSIBLE AND IRREVERSIBLE CELLS

An electrochemical cell may be reversible and irreversible. The reactions in a reversible cell are always in a state of equilibrium and only infinitesimally small currents are drawn from it. A *reversible cell* should satisfy the following conditions:

1. If an emf exactly equal to that of cell is applied from an external source, the chemical reaction taking place in the cell will stop, i.e., no current flows.
2. If the external emf slightly greater than the actual emf of cell is applied to it, the current will begin to flow in opposite direction and the cell reaction gets reversed.
3. If the external emf slightly lower than the actual emf of cell is applied to it, a very small amount of current will flow corresponding to very small amount of chemical change taking place in the cell.

The cell which does not satisfy these conditions is called *irreversible* cell.

A familiar example of the reversible cell is the Daniell cell. When the two electrodes are connected to an external source of emf infinitesimally smaller than the cell emf, the current flows from zinc electrode to the copper electrode and net cell reaction is

$$Zn + Cu^{2+} \rightleftharpoons Zn^{2+} + Cu$$

This process continues as the external opposing emf is infinitesimally smaller than that of the cell. However, if the external emf becomes infinitesimally greater than that of the cell, the current flows in the opposite direction and the cell reaction is reversed. When the external emf becomes exactly equal to that of cell, no current flows and the cell reaction ceases.

On the other hand, a cell consisting of zinc and copper electrodes dipped into a solution of sulphuric acid is irreversible. The cell when connected to an external source of emf slightly smaller than that of the cell, zinc dissolves in sulphuric acid forming zinc sulphate with the evolution of hydrogen. The cell reaction is

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2 \uparrow$$

If the emf of external source is slightly greater than that of the cell, copper goes into solution, hydrogen is liberated at the other electrode and the following reaction takes place

$$Cu + H_2SO_4 \longrightarrow CuSO_4 + H_2 \uparrow$$

It is clear from the above reactions that the cell is not reversible; in each case different sets of products are formed.

10.5. TYPES OF REVERSIBLE ELECTRODES

An electrode consists of a metal and some reactants in the surrounding solution, which are involved in its functioning. Hence each electrode constitutes a half-cell. The reversible electrodes refers to the electrodes of a reversible cell. A combination of any two reversible electrodes gives a reversible cell. The following are four important types of reversible electrodes.

(a) **Electrodes of first kind.** This kind of electrodes includes the following electrodes:

(i) Metal-Metal ion electrodes:

This type of electrode consists of a pure metal rod in contact with a solution of its own ions. It is reversible with respect to its cations and is represented by M/M^{n+}. The half-cell reaction is represented as

$$M \rightleftharpoons M^{n+} + n\bar{e}$$

For example, when Ag wire or foil is immersed in a solution containing Ag^+, the electrode reaction is

$$Ag \rightleftharpoons Ag^+ + \bar{e}$$

Electrode is reversible with respect to Ag^+ ions. Similarly when Zn electrode is immersed in $ZnSO_4$ solution, the half-cell reaction is

$$Zn \rightleftharpoons Zn^{2+} + 2\bar{e}$$

It is reversible with respect to Zn^{2+} ions.

Very active metals like sodium or potassium which react with water cannot be used for designing such electrodes.

(ii) Amalgam electrodes:

Such electrodes are essentially very much similar to the metal-metal ion electrodes. Here the metal is not used in pure form, but instead, is dissolved in mercury to the extent of 10-20% to form an amalgam. In such cases mercury plays no chemical role except that it lowers the activity of the metal. This permits as to design electrodes of even more active metals, e.g., sodium, calcium etc. For example, a sodium amalgam electrode is represented as

$$Na \text{ (in Hg)} \mid Na^+_{(aq)}$$

The electrical contact is made by a platinum wire dipping into the amalgam. This electrode is reversible with respect to Na^+ ion.

(iii) Gas electrodes:

Such electrodes are formed by bubbling an elementary gas over an inert metal dipping into solution containing corresponding ions. For example, the hydrogen gas electrode. It consists of platinum foil exposed to a current of hydrogen gas dipped in HCl solution. It is expressed as

$$\left.\begin{matrix}\text{Pt } H_{2(g)} \\ (P, \text{atm.})\end{matrix}\right| H^+_{(aq)}$$

The corresponding half-cell is represented as

$$\frac{1}{2}H_2(g, P\text{ atm.}) \rightleftharpoons H^+_{(aq)} + \bar{e}$$

The electrode is reversible with respect to H^+ ions.

(b) Electrodes of second kind:

This kind of reversible electrode consists of metal in contact with one of its sparingly soluble salts and a solution of soluble salt having a common anion with the sparingly soluble salt, e.g., a silver-silver chloride electrode it is reversible with respect to Cl^- ions. It consists of Ag-metal in contact with its sparingly soluble salt (AgCl) and and a soluble electrolyte having a common anion (HCl). It many be represented as

$$Ag \mid AgCl_{(s)}, HCl_{(aq)}$$

The electrode reaction is represented as

$$Ag_{(s)} + Cl^- \rightleftharpoons AgCl_{(s)} + \bar{e}$$

Another electrode of this type frequently used in electrochemistry is the *calomel electrode.* It consists of metallic mercury in contact with calomel, Hg_2Cl_2, which in turn is contact with a solution containing Cl^- ions. It may be represented as

$$Hg \mid Hg_2Cl_{2(s)}, KCl_{(aq)}$$

The electrode reaction is represented on

$$Hg_{(\ell)} + Cl^- \rightleftharpoons \frac{1}{2}Hg_2Cl_{2(s)} + \bar{e}$$

The calomel electrode can be quite easily prepared and generally 0.1N or 1.0N or saturated solution of KCl is used. Electrodes of 2nd kind are of much utility, because of their reversibility with respect to anions such as sulfate, oxalate etc. which other wise cannot be obtained directly.

(c) Electrodes of third kind.

This type of electrodes consist of metal, one of its insoluble salts, another insoluble salt of another metal having same anion and the solution of any soluble salt having the cation common to the latter salt. An example of such electrode is

$Pb \mid PbC_2O_{4(s)}, CaC_2O_{4(s)}, CaCl_{2(aq)}$

The electrode reactions are

$$Pb \rightleftharpoons Pb^{2+} + 2\bar{e}$$

$$Pb^{2+} + C_2O_4^{2-} \rightleftharpoons PbC_2O_{4(s)}$$

Thus removal of oxalate ions from the solution causes the dissolution of solid CaC_2O_4 according to the following equilibrium.

$$CaC_2O_4 \rightleftharpoons Ca^{2+} + C_2O_4^{2-}$$

so that the overall reaction is

$$Pb_{(s)} + CaC_2O_{4(s)} \rightleftharpoons Pb\ C_2O_{4(s)} + Ca^{2+} + 2\bar{e}$$

Thus the above electrode system behaves reversible with respect to calcium ions. Such electrodes are used where it is not possible to fabricate electrodes reversible to ions of any active metals.

(d) Electrodes of fourth kind.

This kind of electrodes consist of oxidation-reduction or redox electrodes. No doubt, all electrodes involve oxidation-reduction reaction but the electrodes named redox electrodes include only the electrodes consisting of an inert metal (e.g. platinum, gold) immersed into a solution containing both oxidized and reduced forms of a molecule or ion. The inert metal simply provides electrical contact. The general electrode reaction is

$$\text{Reduced form} \rightleftharpoons \text{oxidized form} + n\bar{e}$$

Common redox half-cells are:

$Pt \mid Fe^{2+}, Fe^{3+}$

$Pt \mid Sn^{2+}, Sn^{4+}$

$Pt \mid Ce^{3+}, Ce^{4+}$

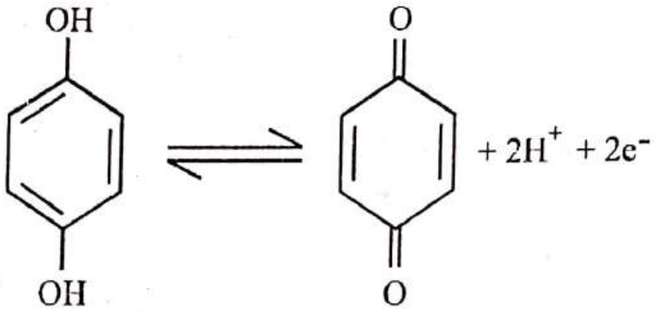
$Pt \mid MnO_4^-, Mn^{2+}$

The gain or loss of electrons by such electrodes is not associated with the liberation or dissolution of the electrode material (metals or gases), but in fact causes a change in the valence of the ions present in the solution.

Certain organic substances in their non-ionized oxidized, and reduced forms also give ion to this type of electrode systems. Most widely used electrode, involving quinone-hydroquinone redox couple is termed as quinhydrone electrode. It consists of Pt-metal dipped into a solution containing hydroquinone (i.e., reduced form) and Q the quinone (oxidized form), the electrode can be represented as

$Pt \mid QH_2\ Q, H^+$

The electrode reaction is



or simply

$$QH_2 \rightleftharpoons Q + 2H^+ + 2e^-$$

10.6. ELECTROMOTIVE FORCE AND ITS MEASUREMENT

When a cell is connected in series with a galvanometer and the circuit is closed, the galvanometer is deflected, indicating that a current is flowing through the circuit. The flow of current from one electrode to the other is evidence for the existence of a potential difference between them. This difference of potential which causes a current to flow from the electrode of higher potential to the one of lower is called the *electromotive force* of the cell. It is abbreviated as emf and is expressed in volts (V).

The most common method of determining the potential difference between any two points in an electric circuit is to connect a voltmeter across the two points. The potential difference or voltage is read then directly from the instrument. A serious objection to the use of voltmeter is that, it draws some current from the cell during measurements. When some current is drawn from the cell reaction products are formed at the electrode surfaces which cause concentration change of the electrolyte around the electrodes. This polarization of the electrodes changes the emf of the cell. Again with appreciable current flow, part of the emf will have to be utilized to overcome the internal resistance of the cell, and hence the potential measured on voltmeter will not be the total cell emf. Hence potential measuring devices like potentiometers which require only small currents are suitable for accurate measurements and other instruments like voltmeter, etc. which draw appreciable currents from the cell are unsuitable for emf measurements.

Potentiometers for emf measurements operate on the *Poggendorff compensation principle*. In this method the unknown emf is opposed by another known emf until the two are equal. Figure 10.3 gives a basic circuit diagam of a direct reading potentiometer. *ab* is the slide wire of uniform cross sectional area having high resistance. A cell W, usually a storage battery of constant emf larger than the emf of the cell to be measured, is connected in series with the resistance across the terminal of resistance wire ab. The cell X of unknown emf is connected to 'a' with poles in the same direction as the cell W. The other terminal of the cell is connected through the galvanometer G to the sliding wire by a double-pole double throw key, D. The position of the terminal is moved along the sliding wire and the rheostat is adjusted until at S′ no current flows through the galvanometer. At this point the potential difference between 'a' and S′ just balances the emf Ex of the cell X. Next the standard cell S.C. with emf Es is connected to the sliding wire by means of D. The null point S on the sliding wire is again determined. The fall in potential along aS′ is exactly compensated by the emf of the standard cell, Es. Since the cross sectional areas of the wire is uniform, hence we have

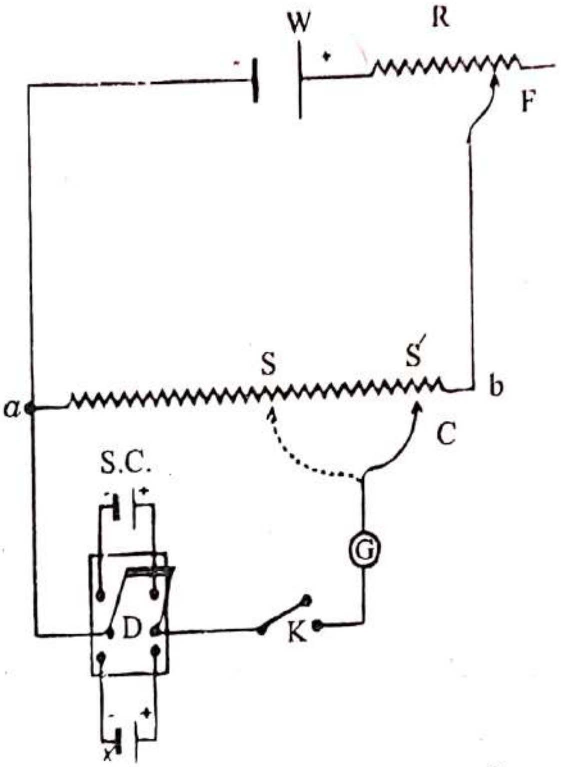


Fig. 10.3. Principle of direct reading potentiometer.

$$\frac{E_X}{E_S} = \frac{\text{Drop of potential from } a \text{ to S}'}{\text{Drop of potential from } a \text{ to S}} = \frac{\text{Length } a\text{S}'}{\text{Length } a\text{S}}$$

Knowing the emf of S.C., we can calculate the emf of experimental cell X.

The standard cell should be capable of giving a constant and reproducible emf. The most widely used standard cell is a Weston Cell (Fig. 10.4). It consists of a H-shaped glass vessel containing in each arm one of the electrodes and filled throughout with the electrolyte. The positive electrode consists of mercury covered with a paste of mercury-mercurous sulphate and the negative electrode is a 12.5% cadmium amalgam. A saturated solution of cadmium sulphate ($CdSO_4 . \frac{8}{3} H_2O$) is placed over the electrode. The cell reactions when it operates spontaneously are:

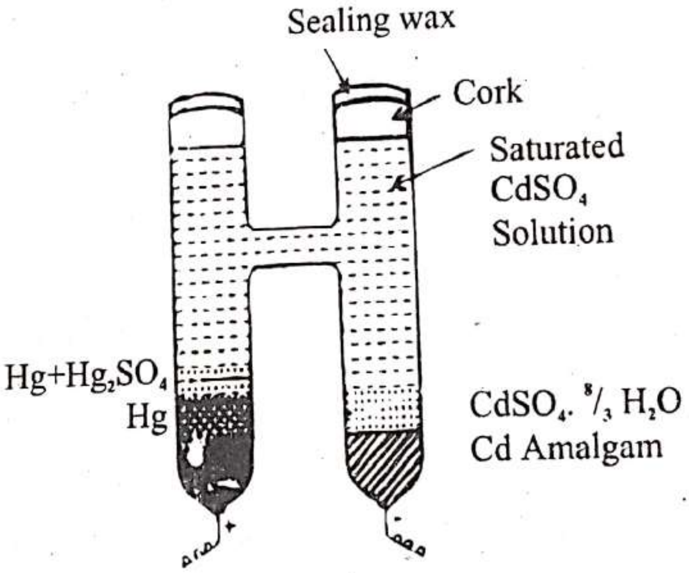


Fig. 10.4. Saturated Weston standard cell

Anode reaction: $Cd(Hg) \rightleftharpoons Cd^{2+} + Hg + 2e^-$

Cathode reaction: $Hg_2SO_4 + 2e^- \rightleftharpoons 2Hg + SO_4^{2-}$

Overall reaction: $Cd(Hg) + Hg_2SO_4 \rightleftharpoons Cd^{2+} + 3Hg + SO_4^{2-}$

The emf of the cell is 1.01832 V at 298 K and varies only slightly with temperature.

10.7. ELECTRODE POTENTIAL

We know that each cell is made up of two electrodes. At one electrode oxidation takes place, i.e., electrons are evolved. At the other electrode reduction takes place, i.e., electrons are taken up. For example, Daniell cell consists of two electrodes; zinc electrode where oxidation takes place and copper electrode where reduction takes place. Each electrode is regarded as a half-cell.

The tendency of an electrode to lose or gain electrons when it is in contact with its own ions in the solution is called *electrode potential* or *single electrode potential*. Thus the electrode potential is the measure of the tendency of an electrode to lose or gain the electrons, when it is in contact with its own ions. Thus we have oxidation and reduction potential.

Oxidation and Reduction Potentials

The cell reaction consists of two half cell reactions, of which one is oxidation reaction and the other is reduction reaction. Electromotive force (emf) of a cell may be regarded as being made up of two single electrode potentials. Their algebraic sum equals to the emf of cell.

$$E_{Cell} = E_{Anode} + E_{Cathode}$$

1. E_{anode} would be the measure of tendency of anode to lose the electrons. Since loss of electrons is oxidation,

$$M \longrightarrow M^{n+} + ne^-$$

the E_{anode} would be called oxidation potential. Hence we can define oxidation potential as the measure of the tendency of an electrode to lose the electrons. It is denoted by E_{oxi}.

2. $E_{cathode}$ stands for the potential electrode at which reduction occurs.

$$M^{n+} + ne^- \longrightarrow M$$

Hence reduction potential is the measure of tendency of electrode to gain the electrons. It is denoted by E_{red}. Since cell reaction is essentially a redox-process, we can also write

$$E_{Cell} = E_{oxi} + E_{red}$$

The reduction potential of an electrode is the same as its oxidation potential with the sign changed.

Standard Electrode Potential

It is defined as the potential of the electrode when all of the ion concentrations are 1.00 M, the temperature is 25°C, and any gases that are involved in the cell reaction are at a pressure of 1 atmosphere. It is denoted by the symbol E°.

Nernst Theory of Electrode Potential

It is well known fact that the ultimate source of emf in a galvanic cell is the chemical reaction which proceeds when a current is flowing. Nernst (1889) proposed a theory to explain the above phenomenon. According to the theory all metallic elements and hydrogen have a tendency to pass into solution in the form of positive ions. This property of the metal is known as *solution pressure* or *solution tension* of the metal and is constant at a given temperature. Due to the migration of positive ions, the metallic electrode is left negatively charged and thus an electrical double layer is set up at the electrode. If zinc is immersed in pure water, Zn^{2+} ions pass into the water under the stress of solution pressure of the metal.

$$Zn \longrightarrow Zn^{2+} + 2e^-$$

The zinc metal, therefore is left with a negative charge due to the migration of Zn^{2+} ions away from it. Hence, there exists a difference of potential between the metal and the liquid. On account of the relatively large magnitude of charge involved, the ions do not move away from the oppositely charged metal, but form an electrical double layer. The formation of double layer prevents the further expulsion of ions from the metal and thus there is rapidly established a state of equilibrium with a definite potential difference termed as the electrode potential.

If the metallic electrode is dipped in a solution of one of its salts, the position becomes slightly different. In such a case, the tendency of the ions is to be deposited on the electrode. This backward reaction is attributed to the osmotic pressure of the ions in the solution. Thus, the standard potential of a metal is equal to the difference between its solution pressure and *osmotic* pressure of the ions. Hence there arises three possibilities:

(i) If the solution pressure is greater than the osmotic pressure the tendency of the metal to lose ions predominates. A potential difference is therefore, set up with the metal left with negative charge with respect to the solution. The net result will be that the positive ions will enter the liquid and leave the metal negatively charged with respect to the solution. For example, Zn, Mn, Cd and alkali metals. (Fig. 10.5a)

(ii) If the solution pressure is less than the osmotic pressure of the metal in the solution, then ions will have greater tendency to leave the solution and get deposited on the metal. In simple words when a metal is placed in a solution of one of its salts, a positive charge would develop on the metal with respect to the solution and a potential difference would be established. Examples are Cu, Ag, Hg and Au. (Fig. 10.5b)

(iii) When the solution pressure becomes equal to that of osmotic pressure, no relative charge is developed and hence no potential difference exists. Such systems are sometimes termed as null electrodes. (Fig. 10.5c)

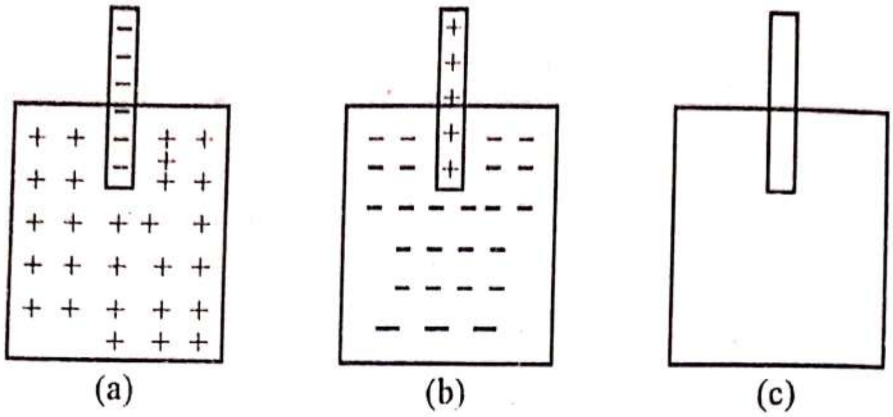


Fig. 10.5 (a) Solution pressure is greater osmotic pressure (b) solution pressure is less than osmotic pressure (c) solution pressure is equal to osmotic pressure.

Measurement of Electrode Potential

Unfortunately there is no way to measure the single electrode potential of an isolated half-cell. All we can measure is the difference that is produced when two half cells are connected. In order to determine single electrode potentials, it would be necessary to couple an electrode with a reference or standard electrode. The potential of the reference electrode is arbitrarily assigned a zero value and the potentials of all other electrodes are then referred to it. Two such reference electrodes are described below:

(a) Standard Hydrogen Electrode (SHE)

A simple type of standard hydrogen electrode is shown in Fig. 10.6.

Gaseous hydrogen at a pressure of 1 atm is bubbled over a platinum electrode that is coated with a very finely divided platinum, which causes the electrode reaction to occur rapidly. This electrode is surrounded by a solution whose temperature is 25°C and in which the hydrogen ion concentration is 1.00M. The half-cell reaction that occurs at the platinum surface is.

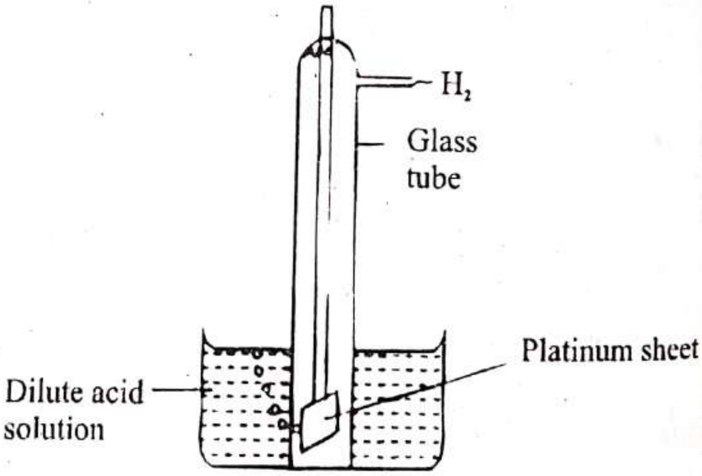


Fig. 10.6. Hydrogen electrode

$$2H^+ \ (aq, 1.00\,M) + 2e^- \rightleftharpoons H_2 \ (g, 1\ atm) \quad E^{O}_{H^+} = 0.00\ V \text{ at } 25°C$$

The double arrows indicate that the reaction is reversible – whether it occurs as oxidation or reduction depends on the potential of half cell with which it is paired. All other potentials expressed on this basis are referred to as potentials on hydrogen scale. The standard electrode potential of any other electrode is then obtained by combining the electrode with the SHE. Since the standard potential of hydrogen electrode is zero, the measured potential is the standard electrode potential of the other electrode. The standard electrode potential is assigned a positive value if this electrode is more positive with respect to SHE and a negative value if it is more negative than the SHE. Such a galvanic cell can be represented as:

$$M \mid M^{n+}(aq) \parallel H^+ \ (M = 1) \mid H_2(g, 1\ atm), Pt$$

If oxidation takes place at $M \mid M^{n+}$ electrode, reactions will be

At metal electrode: $M_{(s)} \rightleftharpoons M^{n+} + ne^-$

At hydrogen electrode: $nH^+ + ne^- \rightleftharpoons n/_2\, H_{2(g)}$

Over all reaction: $M_{(s)} + nH^+ \rightleftharpoons n/_2\, H_{2(g)}$

It is also possible that reduction can take place on metal and oxidation on hydrogen electrode then the electrode reactions will be

At hydrogen electrode: $n/_2\, H_2 \rightleftharpoons nH^+ + ne^-$

At metal electrode: $M^{n+} + ne^- \rightleftharpoons M_{(s)}$

Overall reaction: $n/_2\, H_2 + M^{n+} \rightleftharpoons nH^+ + M_{(s)}$

In the hydrogen electrode platinum is poisoned by the absorbed impurities from the solution and this causes difficulty in its use as it checks the reversibility of the reaction. Moreover, it is difficult to maintain one atmospheric pressure of gas uniformly and the unit activity of the hydrogen ion, so it is usually replaced by the Calomel electrode which is easy to use.

(b) Calomel Electrode

A simple type of calomel electrode generally used in the laboratory is shown in Fig. 10.7. It consists of glass vessel with small quantity of pure mercury at the bottom. The mercury layer is covered with paste of mercurous chloride and is filled with a saturated solution of KCl. A platinum wire is fused in glass tube and a siphon tube is provided for the connection. The electrical contact is made with the other single electrode whose potential is to be determined by means of siphon tube containing a jelly or agar-agar prepared in saturated KCl solution. Such a connecting solution is called *salt bridge*.

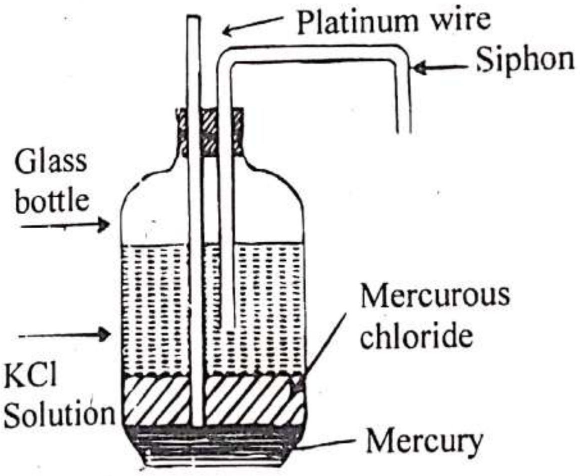


Fig. 10.7 Calomel electrode

The half cell reaction is:

$$Hg_2Cl_2 + 2e^- \rightleftharpoons 2Hg(\ell) + 2Cl^-$$

The potential of the calomel electrode depends upon the concentration of KCl solution. The potentials of calomel electrodes as determined by combination with standard hydrogen electrode are given in Table 10.1.

Table 10.1. Calomel Electrode Potentials

Calomel electrode	Oxidation potential	Reduction potential
Saturated KCl	- 0.2415 volt	+ 0.2415 volt
1 M KCl	- 0.2812 volt	+ 0.2812 volt
0.1 M KCl	- 0.3335 volt	+ 0.3335 volt

Sign of Electrode Potentials

1. According to IUPAC system – the electrode potential is given positive sign if the electrode reaction involves reduction when connected to SHE. For example, when copper electrode is connected with SHE, reduction occurs at copper electrode.

At SHE: $H_{2(g)} \rightleftharpoons 2H^+ + 2e^-$ (oxidation)

At copper electrode: $Cu^{2+} + 2e^- \rightleftharpoons Cu_{(s)}$ (reduction)

$$H_{2(g)} + Cu^{2+} \rightleftharpoons 2H^+ + Cu_{(s)}$$

Hence potential of copper electrode will have positive sign.

That is, $E^0_{(Cu^{2+}/Cu)} = 0.337$ volts

2. The electrode potential is given negative sign, if the electrode reaction involves oxidation, when connected with SHE. For example, when zinc electrode is connected with SHE oxidation occurs at the zinc electrode.

$$Zn_{(s)} + 2H^+ \rightleftharpoons Zn^{2+} + H_{2(g)}$$

Hence the electrode potential of Zn|Zn^{2+} electrode will be negative and is equal to –0.763 volt. The values of oxidation electrode potential and reduction electrode potential are numerically equal but opposite in sign.

An arrangement of electrode systems in order of increasing standard electrode potential (reduction potential) is given in Table 10.2. This is known as standard reduction electrode potential series. In some books, standard oxidation potential series is followed. These series are called *electrochemical series.*

The magnitude of the standard electrode potential is a measure of the tendency for reduction to occur. The reduced form of a half cell higher up in the series has a greater tendency to donate electrons and be oxidized than the reduced form of the half cell which is below it in the series. Similarly, the oxidized form of the half cell lower in the series has a greater tendency to accept electrons and be reduced than the oxidized form of the half cell which is above it in the series.

Table 10.2. standard reduction potentials measured at 25°C

Half-Reaction	E° (volts)
$F_2(g)+2e^- \rightleftharpoons 2F^-(aq)$	+ 2.87
$PbO_2(s)+SO_4^{2-}(aq)+4H^+(aq)+2e^- \rightleftharpoons PbSO_4(s)+2H_2O$	+ 1.69
$2HOCl(aq)+2H^+(aq)+2e^- \rightleftharpoons Cl_2(g)+2H_2O$	+1.63
$MnO_4^-(aq)+8H^+(aq)+5e^- \rightleftharpoons Mn^{2+}(aq)+4H_2O$	+1.49
$PbO_2(s)+4H^+(aq)+2e^- \rightleftharpoons Pb^{2+}(aq)+2H_2O$	+1.46
$BrO_3^-(aq)+6H^+(aq)+6e^- \rightleftharpoons Br^-(aq)+3H_2O$	+1.44
$Au^{3+}(aq)+3e^- \rightleftharpoons Au(s)$	+1.42
$Cl_2(g)+2e^- \rightleftharpoons 2Cl^-(aq)$	+1.36
$O_2(g)+4H^+(aq)+4e^- \rightleftharpoons 2H_2O$	+1.23
$Br_2(aq)+2e^- \rightleftharpoons 2Br^-(aq)$	+1.07
$NO_3^-(aq)+4H+(aq)+3e^- \rightleftharpoons NO(g)+2H_2O$	+0.96
$Ag^+(aq)+e^- \rightleftharpoons Ag(s)$	+0.80
$Fe^{3+}(aq)+e^- \rightleftharpoons Fe^{2+}(aq)$	+0.77
$I_2(s)+2e^- \rightleftharpoons 2I^-(aq)$	+0.54
$NiO_2(aq)+2H_2O+2e^- \rightleftharpoons Ni(OH)_2(s)+2OH^-(aq)$	+0.49
$Cu^{2+}(aq)+2e^- \rightleftharpoons Cu(s)$	+0.34
$SO_4^{2-}(aq)+4H^+(aq)+2e^- \rightleftharpoons H_2SO_3(aq)+H_2O$	+0.17
$2H^+(aq)+2e^- \rightleftharpoons H_2(g)$	0.00
$Sn^{2+}(aq)+2e^- \rightleftharpoons Sn(s)$	-0.14
$Ni^{2+}(aq)+2e^- \rightleftharpoons Ni(s)$	-0.25
$Co^{2+}(aq)+2e^- \rightleftharpoons Co(s)$	-0.28
$PbSO_4(s)+2e^- \rightleftharpoons Pb(s)+SO_4^{2-}(aq)$	-0.36

Half-Reaction	E° (volts)
$Cd^{2+}(aq) + 2e^- \rightleftharpoons Cd(s)$	-0.40
$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$	-0.44
$Cr^{3+}(aq) + 3e^- \rightleftharpoons Cr(s)$	-0.74
$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$	-0.76
$2H_2O + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq)$	-0.83
$Al^{3+}(aq) + 3e^- \rightleftharpoons Al(s)$	-1.66
$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$	-2.37
$Na^+(aq) + e^- \rightleftharpoons Na(s)$	-2.71
$Ca^{2+}(aq) + 2e^- \rightleftharpoons Ca(s)$	-2.76
$K^+(aq) + e^- \rightleftharpoons K(s)$	-2.92
$Li^+(aq) + e^- \rightleftharpoons Li(s)$	-3.05

Since a substance that is reduced is an oxidizing agent, the substances located to the left of the double arrows are all oxidizing agents. The best oxidizing agents are those at the top of the table (e.g., F_2). When one half-reaction occurs as a reduction, another must occur as an oxidation. Substances that are oxidized are reducing agents. reucing agents are located to the right of the double arrows and the best reducing agents are those found at the bottom of the table (e.g., Li).

10.8. CELL POTENTIAL (E_{cell})

The electromotive force (emf) or voltage across the electrodes of a galvanic cell can be attributed to the difference in the tendencies of the two half-cells to undergo reduction. Voltage or emf can be thought of as the force with which an electric current is pushed through a wire. It is measured in terms of an electrical unit called the volt (V). Strictly speaking 1 voltage is a measure of the amount of energy that can be delivered by a Coulomb of electrical charge as it passes through a circuit. A current flowing under an emf of 1 volt can deliver 1 joule of energy per Coulomb.

$$1V = 1\ J/C \tag{10.1}$$

The maximum emf of a galvanic cell is called the cell *potential* (E_{cell}). It is measured with a device that draws negligible current during the measurement. Cell potential depends on the composition of the electrodes and the concentration of the ions in each of half-cells. For reference purpose, the *standard cell potential* (E^0_{Cell}) is the potential of the cell when all the ion concentrations are 1.00 M, temperature is 25°C, and any gases that are involved in the cell reaction are at a pressure of 1 atm.

Cell potentials are rarely large than a few volts. For example, the standard cell potential for the galvanic cell constructed from silver and copper electrodes is only 0.46V and one cell in an automobile battery produces about 2V.

We know that the measured overall cell potential arises from, competition between two half-cells for electrons. Each half-cell reaction has a natural tendency to proceed as reduction, the magnitude of which is expressed by its *reduction potential* or *standard reduction potential* when the temperature is 25°C, concentrations are 1 M and pressure is 1 atm. When two half-cells are connected, the one with larger reduction potential the one with the greater tendency to undergo reduction-acquires electrons from the half-cell with the lower reduction potential, which is therefore forced to undergo oxidation. The measured cell potential actually represents the magnitude of the difference between the reduction potential one of half-cell and reduction potential of the other. In general.

$$E^0_{cell} = \begin{pmatrix} \text{s tan dard reduction} \\ \text{potential of the} \\ \text{subs tan ce reduced} \end{pmatrix} - \begin{pmatrix} \text{S tan dard reduction} \\ \text{potential of the} \\ \text{subs tan ce oxidized} \end{pmatrix} \qquad (10.2)$$

Let us look at the silver-copper cell. From the cell reaction.

$$2Ag^+_{(aq)} + Cu_{(s)} \longrightarrow Cu^{2}_{(aq)} + 2Ag_{(s)}$$

one can see that the silver ion is reduced and copper is oxidized. If we compare the two possible reduction half-reactions.

$$Ag^+_{(aq)} + e^- \longrightarrow Ag_{(s)}$$

$$Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu_{(s)}$$

The one for Ag^+ must have a greater tendency to proceed than one for the Cu^{2+}, because it is the silver ion that is actually reduced. This means that the standard reduction potential of Ag^+ must be larger than the standard reduction potential of Cu^{2+}. Therefore the standard cell potential of Ag-Cu cell is given as

$$E^0_{cell} = E^0_{Ag^+} - E^0_{Cu^{2+}}$$

Unfortunately there is no way to measure the standard reduction potential of an isolated half-cell. All we can measure is the difference that is produced when two half-cells are connected. Therefore, to assign values to various standard reaction potentials, a reference electrode has been arbitrarily chosen and its standard reduction potential has been assigned a value of 0.00 V. The reference electrode is called standard hydrogen electrode (SHE) discussed is the previous section.

Example 10.1. The standard cell potential of a Ag-Cu galvanic cell has a value of 0.64 V. The cell reaction is

$$2Ag^+_{(aq)} + Cu_{(s)} \longrightarrow 2Ag_{(s)} + Cu^{2+}_{(aq)}$$

The reduction potential of Cu^{2+}, $E^o_{Cu^{2+}}$ is 0.34 V. What is the value of $E^0_{Ag^+}$, the reduction potential of Ag^+?

Solution:

The substance which is reduced is Ag^+, which means that Cu is oxidized.

$$E^0_{cell} = E^0_{Ag^+} - E^0_{Cu^{2+}}$$

$$0.46V = E^0_{Ag^+} - 0.34V$$

$$E^0_{Ag^+} = 0.46 + 0.34$$

$$= 0.80\ V$$

Example 10.2. What would be the cell reaction and standard cell potential of a galvanic cell employing the following half-reactions?

$$Al^{3+}_{(aq)} = 3e^- \rightleftharpoons Al_{(s)} \qquad E^9_{Al^{3+}} = -1.66v$$

$$Cu^{2+}_{(aq)} + 2e^- \rightleftharpoons Cu_{(s)} \qquad E^0_{Cu^{2+}} = 0.34v$$

Which half-cell would be anode?

Solution:

In the above reactions Cu^{2+} is reduced cell Al^{3+} is oxidized. The overall cell reactions an given as

$$3\left[Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu_{(s)}\right]3$$

$$2\left[Al_{(s)} \longrightarrow Al^{3+}_{(aq)} + 3e^-\right]$$

$$3Cu^{2+}_{(aq)} + 2Al_{(s)} \longrightarrow 3\ Cu_{(s)} + 2Al^{3+}_{(aq)}$$

The anode in the cell is aluminum, because oxidation takes place at this electrode.

$$E^0_{cell} = E^0_{Cu^{2-}} - E^0_{Al^{3+}}$$

$$= 0.34V - (-1.66V)$$

$$= 2.00V$$

Example. 10.3. Determine wither the following reactions are spontaneous as written. If they are not give the reaction that is spontaneous.

(i) $Cu_{(s)} + 2H^+_{(aq)} \longrightarrow Cu^{2+}_{(aq)} + H_{2(s)}$

(ii) $3Cu_{(s)} + 2NO^-_{3(aq)} + H^+_{(aq)} \longrightarrow 3Cu^{2+}_{(aq)} + 2NO_{(g)} + 4H_2O$

Solution

(i) The half-cell reactions involved in this reaction are

$$Cu_{(s)} \longrightarrow Cu^{2+}_{(aq)} + 2e^-$$

$$2H^+_{(aq)} + 2e^- \longrightarrow H_{2(g)}$$

The H^+ is reduced and Cu is oxitized. Therefore

$$E^0_{Cu} = E^0_{H} - E^0_{Cu^{2+}}$$

$$= (0.00V) - (0.34V)$$

$$= -0.34V$$

The calculated cell potential is negative and therefore reaction (i) is not spontaneous. The spontaneous reaction is

$$H_{2(s)} + Cu^{2+}_{(aq)} \longrightarrow Cu_{(s)}, + 2H^+_{(aq)}$$

(ii) The half-reactions involved are

$$Cu_{(s)} \longrightarrow Cu^{2+}_{(aq)} + 2e^-$$

$$NO^-_{3(aq)} + 4H^+_{(aq)} + 3e^- \longrightarrow NO_{(g)} + 2H_2O$$

The Cu is oxidized while NO_3^- is reduced.

$$E^0_{cell} = E^0_{NO_3^-} - E_{Cu^{2+}}$$

$$= (0.96V) - (0.34V)$$

$$= 0.62V$$

Since the calculated cell potential is positive, the reaction is spontaneous in the forward direction.

10.9. ELECTROCHEMICAL CONVENTIONS AND NOTATIONS

In order to represent a cell the usual convention is to write the electrode (with reduction potential E_R) at which reduction ($M'^+ + e^- \rightleftharpoons M'$) occurs on the right hand side and electrode (with reduction potential E_L) at which oxidation ($M \rightleftharpoons M^+ + e^-$) occurs on the left hand side. The cell is obtained by combining the two half cell and is denoted as

$$M \mid M^+ \parallel M'^+ \mid M'$$

In this symbolism the single vertical line indicates a phase boundary and the two vertical lines denote that the solutions are connected by a salt bridge eliminating the liquid junction potential. In this conventional representation the activities of the species must also be specified and the cell should be written as

$$M \mid M^+(a_M^+) \| M'^+(a_{M'}^+) \mid M'$$

The overall cell reaction is the algebraic sum of the reactions taking place at each electrode.

Reaction at the right electrode: $M'^+ + e^- \rightleftharpoons M'$

Reaction at the left electrode: $M \rightleftharpoons M^+ + e^-$

Cell reaction is $M'^+ + M \rightleftharpoons M' + M^+$

The emf of the cell is obtained by subtracting the electrode potential of the left hand electrode from that of right hand electrode, e.g.,

$$E_{Cell} + E_R - E_L \tag{10.3}$$

In the standard state, the activity of each species is unity, hence Eq. 10.3 gives the standard potential of the cell.

$$E^0_{Cell} = E^0_R - E^0_L \tag{10.4}$$

For the above cell, emf is positive if E^0_R is greater than E^0_L. The cell reaction is spontaneous and the electron flows through the external circuit from left hand electrode to the right hand electrode. Conversely. If E^0_{Cell} is negative, the cell as denoted will not operate spontaneously, instead the cell reaction would now occur in the opposite direction viz. from right to left hand side. However if the concentration of the electrolytes are so adjusted that E^0_{Cell} is zero, then there is no tendency for the reaction to occur from left to right or vice versa. The cell is in a state of equilibrium.

Example 10.4. What is the cell reaction and cell emf at 298K of the cell?

$$Zn \mid Zn^{2+}(a = 1) \| Pb^{2+}(a = 1) \mid Pb$$

Give $E^0_{Zn^{2+}/Zn} = -0.762V$ and $E^0_{(Pb^{2+}/Pb)} = -0.126V$

Solution:

The cell reactions are:

Left hand electrode oxidation: $Zn \rightleftharpoons Zn^{2+}(a = 1) + 2e^-$

Right hand electrode reduction: $Pb^{2+}(a = 1) + 2e^- \rightleftharpoons Pb$

Overall cell reaction: $Zn + Pb^{2+}(a = 1) \rightleftharpoons Zn^{2+}(a = 1) + Pb$

$$\begin{aligned} E^0_{Cell} &= E^0_R - E^0_L \\ &= -0.126 + 0.762 \\ &= +0.636V \end{aligned}$$

10.10. THERMODYNAMIC ASPECTS OF CELL POTENTIAL

(a) Free Energy and EMF of a Cell Reaction

In a reversible electrochemical cell if an infinitesimal amount of current is drawn from or allowed to pass through the cell, the reversible electrical work at constant temperature and pressure is maximum and is equal to the product of voltage and quantity of electricity. If in a cell n equivalents of reactants are converted into the products, then the quantity of electricity that flows through the cell is nF, where F is the Faraday constant and is equal to 96500 coulombs per equivalent. if this amount of charge is transported through the cell of emf E volts, the amount of electrical work done by the cell is

$$\text{Net electrical work} = nFE \qquad (10.5)$$

Since cell is reversible, this work represents maximum work and since electrical work does not involve mechanical work resulting from volume change, it may be taken as equal to change in free energy (ΔF) accompanying the cell reaction.

$$\text{Decrease in free energy} = \text{Electrical work done}$$

$$-\Delta F = nFE$$

or

$$\Delta F = -nFE \qquad (10.6)$$

This equation gives the relationship between free energy change and emf of cell.

The criteria of spontaneity of a cell reaction in terms of ΔF or E are given in Table 10.3.

Table 10.3. Criteria of Spontaneity in Terms of ΔF and E

Reaction	Magnitude of ΔF	Magnitude of E
Spontaneous	$\Delta G < 0$	$E > 0$
Non-spontaneous	$\Delta G > 0$	$E < 0$
Equilibrium	$\Delta G = 0$	$E = 0$

If we are dealing with standard cell potential (E^0_{cell}) we can calculate the standard free energy change (ΔF°)

$$\Delta F^\circ = -nFE^\circ \qquad (10.7)$$

Equation (10.7) is the bridge between electrochemistry and thermodynamics and is very useful to calculate the free energy change in a chemical reaction simply by measuring the cell potential. A reaction can proceed spontaneously at constant temperature and pressure if ΔF is negative and this can happens only if E is positive, i.e., the reaction proceeds in the forward direction. If ΔF is positive and E is negative, the reaction will be non-spontaneous, i.e., it will occur in the reverse direction. If both ΔF are E and zero, this the reaction is at equilibrium.

Example 10.5. calculate ΔF° for the following reaction given that its standard cell potential is 0.320V at 25°C.

Solution:

$$NiO_2 + 2Cl^- + 4H^+ \longrightarrow Cl_2 + Ni^{2+} + 2H_2O$$

Since two Cl^- ions are oxidized to Cl_2, two electrons are transferred.

$$\Delta F^\circ = -nFE^\circ$$
$$= -2 \times 96500 \times 320$$
$$= -\ 61{,}800 J$$
$$= -\ 61.8\ kJ$$

(b) Cell potential and Equilibrium Constant

One of the most useful applications of electrochemistry is the determination of equilibrium constants. We know that

$$\Delta F^\circ = -R \ln Kc \qquad (10.8)$$

According to Eq. (10.7) we also know that

$$\Delta F^\circ = -nFE^\circ$$

Therefore, E° and equilibrium constant are also related. Equalizing the R.H.S. of the above two equations.

$$-nFE^\circ = -RT \ln Kc$$

$$E^\circ = \frac{RT \ln Kc}{nF}$$

or $$E^\circ = \frac{2.303RT \log Kc}{nF} \qquad (10.9)$$

At 25°C, all the constant, can be combined to give

$$E^\circ = \frac{0.0592 \log Kc}{n} \qquad (10.10)$$

The constant 0.0592 has the units joule, divided by coulombs which is volts, n is the number of moles of electron transferred during the cell reaction.

Example 10.6. Calculate Kc for the reaction in example 10.5.

Solution:

The reaction had $E^\circ = 0.320V$ and $n = 2$

$$E^\circ = \frac{0.0592}{n} \log Kc$$

$$0.320 = \frac{0.0592}{2} \log Kc$$

$$\log Kc = \frac{2 \times 0.320}{0.0592} = 10.8$$

Taking the antilog give

$$Kc = 6 \times 10^{10}$$

(c) Relation between Cell potential and Entropy

According to thermodynamics, F,H and S are inter-related as follows:

$$F = H - TS$$

Where F = Gibbs free energy
H = Enthalpy
S = Entropy
T = Temperature

For a given change at constant temperature, the equation becomes

$$\Delta F = \Delta H - T\Delta S$$

or $$\Delta F - \Delta H = -T\Delta S \qquad (10.11)$$

According to Gibbs Helmholtz equation

$$\Delta F = \Delta H + T\left(\frac{\partial(\Delta F)}{\partial T}\right)_P$$

or $$\Delta F - \Delta H = T\left(\frac{\partial(\Delta F)}{\partial T}\right)_P \qquad (10.12)$$

Comparing Eqs. 10.11 and 10.12, we get

$$-T\Delta S = T\left(\frac{\partial(\Delta F)}{\partial T}\right)_p$$

or $$\Delta S = -\left(\frac{\partial(\Delta F)}{\partial T}\right)_p \qquad (10.13)$$

Bur we know that $\Delta F = -nFE$

Substituting the value of ΔF into Eq. 10.13, we have

$$\Delta S = nF\left(\frac{\partial E}{\partial T}\right)_p \qquad (10.14)$$

Equation 10.14 gives the relation between entropy change and cell potential.

(d) Relation between cell potential and Enthalpy.

According to Gibbs-Helmholtz Equation

$$\Delta F = \Delta H + T\left(\frac{\partial(\Delta F)}{\partial T}\right)_p$$

But $\Delta F = -nFE$

Substituting the value of ΔF, we get

$$-nFE = \Delta H + T\left(\frac{\partial(-nFE)}{\partial T}\right)_p$$

$$-nFE = \Delta H - nFT\left(\frac{\partial E}{\partial T}\right)_p$$

or $$\Delta H = nFT\left(\frac{\partial E}{\partial T}\right)_p - nFE$$

or $$\Delta H = nF\left[T\left(\frac{\partial E}{\partial T}\right)_p - E\right] \qquad (10.15)$$

The quantity $\left(\frac{\partial E}{\partial T}\right)_p$ is the temperature coefficient of the cell. Eq. (10.15) permits the calculation of heat of reaction (enthalpy change) form the measured emf of the cell provided the temperature coefficient of the cell is known.

Example 10.7. The measured cell potential (emf) of a standard cadmium cell is 1.01832V at 298K. The temperature conflict of the cell is -5.0×10^{-5}V K^{-1}. Calculate ΔF, ΔH and ΔS for the reaction.

Solution:

n = 2 equivalents per mole

F = 96500 coulombs

E = 1.01832 V

$$\left(\frac{\partial E}{\partial T}\right)_P = -5.0\times 10^{-5}\,V\,K^{-1}$$

$$\Delta F = -nFE$$
$$= -(2)\times(96500)\times(1.01832)$$
$$= -196.535\ kJ\ mol^{-1}$$

$$\Delta S = nF\left(\frac{\partial E}{\partial T}\right)_P$$
$$= (2)\times(96500)\times(-5.0\times 10^{-5})$$
$$= -0.65\ JK^{-1}ml^{-1}$$

$$\Delta H = nF\left[T\left(\frac{\partial E}{\partial T}\right)_P - E\right]$$

$$= 2\times 96500\,[298\times(-5.0\times 10^{-5}) - 1.01832] = -199.388\ kJ\ mol^{-1}$$

10.11. THERMODYNAMICS OF ELECTRODE POTENTIAL – NERNST EQUATION

The electrode potential and the emf of a cell depend on the nature of the electrode temperature and the activities of the ions in the solution. The variation of electrode and cell potentials with the activities of the ions in solution can be obtained from thermodynamic considerations. For a general reaction such as

$$aA + bB \rightleftharpoons lL + mM$$

Occurring in the cell, the Gibbs free energy change is given by the equation

$$\Delta F = \Delta F^\circ + RT \ln \frac{a_L^l . a_M^m}{a_A^a . a_B^b} \qquad (10.16)$$

Where 'a' s represent the activities of reactants and products under a given set of conditions and ΔF° refers to the free energy change for the reaction in the standard state, i.e., when the activities of reactants and products are unity. On substituting the value of $\Delta F = -nFE$ and $\Delta F^\circ = -nFE^\circ$ in equation (10.16), we get

$$-nFE = -nFE^\circ + RT \ln \frac{a_L^l . a_M^m}{a_A^a . a_B^b}$$

Dividing the above equation throughout by –nF, we get

$$E = E^\circ - \frac{RT}{nF} \ln \frac{a_L^l . a_M^m}{a_A^a . a_B^b} \qquad (10.17)$$

Equation 10.17 is known as Nernst equation and gives the dependence of electrode or cell potential in terms of activities of the reactants and products. The quantity E° is known as the standard emf of the cell and is the cell potential when the activities are all unity. At a given temperature, E° is constant and characteristics of the electrode or the cell. At 298 K, equation (10.17) reduces to

$$E = E^\circ - \frac{(8.314)(298)(2.303)}{n(96500)} \log K_C$$

or $$E = E^\circ - \frac{0.0592}{n} \log K_C \qquad (10.18)$$

Example 10.8. What is the potential of copper-silver cell of Ag^+ concentration is 1.0×10^{-3} M and Cu^{2+} concentration is 1.0×10^{-4} M. The standard potential of the cell is 0.46V and the cell reaction is

$$2Ag^+(aq) + Cu(s) \longrightarrow 2Ag(s) + Cu^{2+}(aq)$$

Solution

According to Nernst equation, the equilibrium constant of this reaction is given as

$$K_c = \frac{[Cu^{2+}]}{[Ag^+]^2}$$

$$E = E^\circ - \frac{0.0592}{n} \log K_c$$

$$E = 0.46 - \frac{0.0592}{2} \log \frac{1.0 \times 10^{-4}}{(1.0 \times 10^{-3})^2}$$

$$E = 0.46 - 0.0296 \log (1.0 \times 10^2)$$

$$E = 0.46 - 0.0296\ (2.00)$$

$$E = 0.46 - 0.0592$$

$$E = 0.40\ V$$

10.12. CONCENTRATION CELLS

The cells in which the electrical energy is produced due to physical transfer of material from one concentration to another, are called concentration cells.

or

The cells in which emf is produced due to decrease in free energy accompanying the physical transfer of material from one part of the cell to another part are called concentration cells. The difference in concentration may be in the electrode material or the electrolyte. On this basis, the concentration cells are of two types.

(i) Electrode concentration cells

(ii) Electrolyte concentration cells

(i) Electrode Concentration Cells: The concentration cells in which electrode of same material, having different concentrations, are dipped in the solution of the same electrolyte, are called electrode concentration cells. These may be of two types:-

Cells with Amalgam Electrodes:

In these cells, the concentration of electrode materials can be varied taking their amalgams, i.e., solution of metal electrode in mercury. For example,

$$\underset{a_1}{Zn - Hg} \mid ZnSO_4 \mid \underset{a_2}{Zn - Hg}$$

In order to get different concentrations of two electrodes,, zinc metal is dissolved in mercury with different activities. When the cell operates, zinc is converted into zinc ions at left hand electrode.

$$Zn(a_1) \longrightarrow Zn^{2+} + 2e^-$$

and emf is given by

$$E_1 = E^0_{Zn} - \frac{RT}{2F} \ln \frac{a_{Zn^{2+}}}{a_1} \tag{10.19}$$

Similarly, zinc ions are converted into zinc metal at right hand electrode, i.e.,

$$Zn^{2+} + 2e^- \longrightarrow Zn(a_2)$$

and emf is given as

$$E_2 = E^0_{1\,Zn} - \frac{RT}{2F} \ln \frac{a_2}{a_{Zn^{2+}}} \tag{10.20}$$

In this cell, the net process is

$$Zn(a_1) = Zn(a_2)$$

and the total emf is given by

$$E = E_1 + E_2 \tag{10.21}$$

Substituting the values of E_1 and E_2 from Eqs. (10.19) and (10.20) in Eq(10.21), we get

$$E = E^0_{Zn} - \frac{RT}{2F} \ln \frac{a_{Zn^{2+}}}{a_1} + E^0_{1\,Zn} - \frac{RT}{2F} \ln \frac{a_2}{a_{Zn^{2+}}}$$

When $E^0_{Zn} = E^0_{1\,Zn}$

$$\therefore \quad E = -\frac{RT}{2F} \ln \frac{a_{Zn^{2+}}}{a_1} - \frac{RT}{2F} \ln \frac{a_2}{a_{Zn^{2+}}}$$

$$E = -\frac{RT}{2F} \ln \frac{a_2}{a_1}$$

$$E = \frac{RT}{2F} \ln \frac{a_1}{a_2} \tag{10.22}$$

From equation (10.22), it follows that the emf of the cell is dependent upon the activity ratio of the two amalgams and not at all on the activity of Zn^{2+} ions in the solution.

Cells with Gaseous Electrodes:

In these cells the electrodes are made up of gas material maintained at different partial pressures and being dipped in the solution of gas ions. An example, of this is a cell in which two hydrogen electrodes at partial pressures P_1 and P_2 are dipped in the solution of H^+ ions of activity a_{H^+}.

$$H_2(Pt)\,|\,\text{Solution of } H^+ \text{ ions}\,|\,H_2(Pt)$$

When the cell operates, the oxidation will take place at the negative electrode

$$\frac{1}{2}H_2(P_1) \rightleftharpoons H^+ + e^-$$

and emf of the cell may be given as

$$E_1 = E^0_{H_2} - \frac{RT}{nF} \ln \frac{a_{H^+}}{P_1^{1/2}} \tag{10.23}$$

But $E^0_{H_2} = 0$, and n = 1, therefore, equation (10.23) becomes as

$$E_1 = -\frac{RT}{F} \ln \frac{a_{H^+}}{P_1^{1/2}} \tag{10.24}$$

Similarly, the cell reaction taking place at positive electrode in represented as:

$$H^+ + e^- \rightleftharpoons \frac{1}{2}H_2(P_2)$$

and emf may be given as

$$E_2 = -\frac{RT}{F} \ln \frac{P_2^{1/2}}{a_{H+}} \tag{10.25}$$

The net process in this cell is

$$E = E_1 + E_2 \tag{10.26}$$

Substituting the values of E_1 and E_2 into eq. (10.26), we get

$$E = -\frac{RT}{F} \ln \frac{a_{H^+}}{P_1^{1/2}} - \frac{RT}{F} \ln \frac{P_2^{1/2}}{a_{H^+}}$$

$$E = -\frac{RT}{F} \ln \left(\frac{P_2}{P_1}\right)^{1/2}$$

$$E = -\frac{RT}{2F} \ln \left(\frac{P_2}{P_1}\right) \tag{10.27}$$

From equation (10.27), it follows that the emf of this cell depends upon the partial pressure of hydrogen and is independent of the activity of the solution containing H^+ ions.

(ii) Electrolyte Concentration Cells: The cells in which the two electrodes are of same material and dipped in two solutions of the same electrolyte, though of different concentrations, are called electrolyte concentration cells. The two solutions may be in actual contact or not. Depending on this we have two types of electrolyte concentration cells.

Concentration Cells without Transport

The concentration cells, in which the two electrolyte solutions are not in direct contact and the transfer of ions from one electrolyte solution to the other does not take place directly, is called concentration cell without transport or transference & liquid junction. The emf arises from difference in concentrations of electrolyte solutions.

Let us consider one cell having the electrodes reversible with respect to H^+ and Cl^- as:

$$H_2\,(1\text{ atm.})\ HCl\,(a_1)\ AgCl\,(s)\,|\ Ag$$

When the cell starts functioning, the hydrogen at the left hand electrode dissolves to form hydrogen ions, whereas from silver chloride, silver is deposited at the right hand electrode as represented by

$$\frac{1}{2}H_2\,(1\text{atm.}) \rightleftharpoons H^+ + e^-$$

$$AgCl(s) + 1e^- \rightleftharpoons Ag + Cl^-$$

The net cell reaction may be obtained by adding the above two half-cell reactions.

$$\frac{1}{2}H_2\,(1\text{ atm.}) + AgCl(s) \rightleftharpoons HCl(a_1) + Ag(s)$$

As H^+ ions are formed in hydrochloric acid solution activity, then emf of the cell may be taken as

$$E_1 = -E^o\,\frac{RT}{F}\,\ln a_1 \qquad (10.28)$$

Let us consider the cell with different activities of HCl. This is represented by

$$H_2\,(1\text{ atm.})\ |\ HCl\,(a_2)\ AgCl(s)\ |\ Ag$$

As proved earlier, the net reaction occurring in the cell is

$$\frac{1}{2}H_2\,(1\text{ atm.}) + AgCl(s) \rightleftharpoons HCl(a_2) + Ag(s)$$

The emf for this cell is

$$E_2 = E^o - \frac{RT}{F}\,\ln a_2 \qquad (10.29)$$

Now connect the two cells containing HCl of activities a_1 and a_2 with emf's E_1 and E_2 in opposition. The resulting cell will be

$$H_2\,(1\text{ atm.})\ |\ HCl\,(a_1),\ AgCl(s)\,|\ Ag\ |\ AgCl(s),\ HCl\,(a_2)\ |\ H_2\,(1\text{ atm.})$$

Since both the simple cells are combined oppositely, the overall cell reaction of this concentration cell without transport will be the difference of above cell reaction. That is

$$\frac{1}{2}H_2\,(1\text{ atm.}) + AgCl(s) \rightleftharpoons Ag(s) + HCl\,(a_1)$$

$$\frac{1}{2}H_2\,(1\text{ atm.}) + AgCl(s) \rightleftharpoons Ag(s) + HCl\,(a_2)$$

Substracting $0 + 0 \rightleftharpoons HCl(a_1) - HCl(a_2)$

or $HCl(a_2) \rightleftharpoons HCl(a_1)$

Now the emf of the cell is

$$E = E_1 - E_2$$

$$E = \left(E^\circ - \frac{RT}{F}\ln a_1\right) - \left(E^\circ - \frac{RT}{F}\ln a_2\right)$$

$$E = \frac{RT}{F}\ln\frac{a_2}{a_1} \tag{10.30}$$

As $a_2 > a_1$, there occurs a transfer of electrolyte from concentrated to dilute solution which follows from equation (10.30)

Concentration Cells with Transport

The cells in which two solutions containing the same electrolyte but at different concentrations are in direct contact and the identical electrode reversible to either ions of the electrolyte are placed in these solutions are called *concentration cells with transport or with liquid junction*. In these cells the liquid junction potential at the interface of two solutions is taken into account.

The typical concentration cell with transport is

$$Pt, H_2(1\text{ atm.})|\,HCl(a_1) \,\vdots\vdots\, HCl(a_2)\,|\,H_2(1\text{ atm.}), Pt$$

In the above cell the two solutions of HCl are in contact with each other and thus there is a direct transfer of HCl from the more concentrated solution (a_2) to the less concentrated solution (a_1). In general, whenever two solutions of the electrolyte of two concentrations are placed together and the electrode reversible with respect to one of the ions of the electrolyte is kept is each solution, then a concentration cell with transport is obtained. In the above cell, the double dotted lines represent the liquid junction potential the electrode reactions for each faraday of electricity drawn from the cell are:

Left electrode (oxidation): $\frac{1}{2}H_2 \rightleftharpoons H^+(a_1) + e^-$

Right electrode (reduction): $H^+(a_2) + e^- \rightleftharpoons \frac{1}{2}H_2$

Overall cell reaction is given by adding the above two equation.

$$H^+(a_2) \rightleftharpoons H^+(a_1) \tag{10.31}$$

Hence, when current flows, the H^+ ions generated at the left electrode are consumed at the right electrode. Since the solutions ore in direct contact with each other, the ions (H^+ and Cl^-) are free to move from one solution to the other with the flow of current in the cell. This current in the cell is composed, of course, not of free electrons but of negative chloride ions (Cl^-). Moving from right to left and positive ions (H^+) moving across the liquid junction from left to right.

Suppose t_c and t_a are the transport numbers of H^+ and Cl^- ions respectively. for the passage of one faraday of electricity through the cell, the tc faraday is carried by tc gram ion of hydrogen from left to right, i.e., from the solution of activity a_1 to a_2. Thus we can write

$$t_c.\, H^+ (a_1) = t_c.\, H^+ (a_2) \tag{10.32}$$

As $\quad t_c + t_a = 1$ or $t_c = 1 - t_a$

$$\therefore\ (1 - t_a)\, H^+ (a_1) = (1 - t_a)\, H^+ (a_2) \tag{10.33}$$

Also t_a faraday of electricity will be carried by t_a g of chloride ion from right to left, i.e., from the solution of activity a_2 to a_1, thus we can write

$$t_a\ Cl^- (a_2) = t_a\ Cl^- (a_1) \tag{10.34}$$

Therefore in order to obtain the net transfer of material, we must add equations (10.31) (10.33) and (10.34)

$$H^+(a_2) + (1-t_a)H^+(a_1) + t_a.Cl^-(a_2) = H^+(a_1) + (1-t_a).H^+(a_2) + t_a.Cl^-(a_1)$$

but $\quad t_a + t_c = 1, \quad \therefore\ t_c = 1 - t_a$

$$H^+(a_2) + H^+(a_1) - t_a.\, H^+(a_1) + t_a.Cl^-(a_2) = H^+(a_1) + H^+(a_2) - t_a.\, H^+(a_2) + t_a.Cl^-(a_1)$$

$$-t_a.\, H^+(a_1) + t_a.Cl^-(a_2) = -t_a.\, H^+(a_2) + t_a.\, Cl^-(a_1).$$

$$t_a.H^+(a_2) + t_a.Cl^-(a_2) = t_a.\, H^+(a_1) + t_a.\, Cl^-(a_1)$$

$$t_a\,[H^+(a_2) + Cl^-(a_2)] = t_a\,[H^+(a_1) + Cl^-(a_1)]$$

$$t_a.\, HCl\,(a_2) = t_a.\, HCl\,(a_1) \tag{10.35}$$

Equation (10.35) shows that t_a equivalents of HCl are transferred from solution of activity a_2 to solution of activity a_1 for the passage of any faraday of electricity.

The emf of the complete cell is given by

$$E = E_1 - E_2$$

$$E = \left(E^\circ - \frac{RT}{F} \ln a_1^{t_a}\right) - \left(E^\circ - \frac{RT}{F} \ln a_2^{t_a}\right)$$

$$E = -\frac{RT}{F} \ln a_1^{t_a} + \frac{RT}{F} \ln a_2^{t_a}$$

$$E = -\frac{RT}{F} \ln \left(\frac{a_1}{a_2}\right)^{t_a}$$

$$E = -t_a \frac{RT}{F} \ln \frac{a_1}{a_2}$$

$$E = t_a \frac{RT}{F} \ln \frac{a_2}{a_1} \qquad (10.36)$$

Thus is such cell the emf of the cell depends upon the transference number of the ions other than to which the electrode is reversible. Such cells therefore, provide very convenient means of determining the transference number of the ions other than the one to which the electrodes are reversible, through the emf measurements.

10.13. LIQUID JUNCTION POTENTIAL

When two electrolytic solutions of different concentrations are brought in contact with one another, a potential difference develops at the junction of two solutions. This potential difference is called *liquid junction potential* or *diffusion potential.*

When two salt solutions of different concentrations are placed in contact with one another, the ions from the concentrated solution will tend to diffuse into the dilute one. The rate of diffusion of each ion is approximately proportional to the speed of the ions in the electric field. The liquid junction potential arises mainly due to unequal rates of diffusion of ions across in migration velocities of ions. Let us consider a cell where two hydrogen electrodes are dipped in two solutions of HCl at different concentrations.

$$\underset{\text{I}}{\text{Pt}, H_{2(g)} \,|\, \text{HCl}\,(a_1)} \;\vdots\; \underset{\text{II}}{\text{HCl}(a_2) \,|\, H_{2(g)}\text{Pt}} \qquad (a_1 > a_2)$$

There will be diffusion of electrolyte from solution of higher concentration to that of lower concentration. Because different ions have different velocities, they tend to diffuse across the boundary (junction) at different speeds. Both H^+ and Cl^- ions diffuse from concentrated solution to dilute solution. The ionic velocity of H^+ ions is greater than that of Cl^-. So H^+ ions will diffuse more rapidly from a_1 to a_2. The dilute solution in II compartment will thus become more positively charged with respect to solution in I. As a result of this, concentrated solution (I) is left with excess of Cl^- ions and thus acquires negative charge. Hence, an electrical double layer of +ive and –ive charges is formed at the junction of two solutions and a potential difference is developed at the junction. It is called *liquid junction potential.* Thus we can say that

(i) The liquid junction potential is due to difference is the velocity of ions.

(ii) The magnitude of liquid junction potential depends upon the relative speed of ions.

(iii) If two ions are moving with same speed, there will be no liquid junction potential.

(iv) The liquid junction potential cannot be measured directly, but it can be calculated.

Determinations of Liquid Junction Potential

The liquid junction potential can be calculated by considering the equations derived for the emf of a concentration cell with and without transport. Let us consider the solutions of some uni-univalent electrolyte, i.e., KCl

$$\text{KCl}\ (a_1) = \text{KCl}\ (a_2)$$

Adopting the usual convention for the positive emf that the left hand electrode is the source of electrons. If one faraday of electricity is passed through the cell, t_c g ion of cation (i.e., K^+) migrates from left to right and t_a g of anion (Cl^-) from right to left. If an assumption is made that the transference numbers are assumed to be independent of concentrations, then the free energy change for the passage of one faraday of electricity can be calculated.

The free energy change for positive ion in the left compartment is given by

$$\Delta F_1 = t_c\ RT\ \ln \frac{(a_+)_2}{(a_+)_1}$$

and the free energy change for negative ion in the right compartment is as follows:

$$\Delta F_2 = t_a\ RT\ \ln \frac{(a_-)_1}{(a_-)_2}$$

The net change in free energy is given by

$$\Delta F = \Delta F_1 + \Delta F_2$$

$$\Delta F = t_c\ RT\ \ln \frac{(a_+)_2}{(a_+)_1} + t_a\ RT\ \ln \frac{(a_-)_1}{(a_-)_2} \qquad (10.37)$$

If E_J is the liquid-junction potential, it means that the electrical work done is nE_JF.

$$\Delta F = -nE_JF \qquad (10.38)$$

But $\quad n = 1$

$$\Delta F = -E_JF$$

$$E_J = -\Delta F/F \qquad (10.39)$$

Substitution the value of ΔF from equation (10.37), we get

$$E_J = -t_c \frac{RT}{F} \ln \frac{(a_+)_2}{(a_+)_1} - t_a \frac{RT}{F} \ln \frac{(a_-)_1}{(a_-)_2}$$

$$E_J = -t_c \frac{RT}{F} \ln \frac{a_2}{a_1} - t_a \frac{RT}{F} \ln \frac{a_1}{a_2} \qquad (a = a+ = a-)$$

$$E_J = -t_c \frac{RT}{F} \ln \frac{a_2}{a_1} + t_a \frac{RT}{F} \ln \frac{a_2}{a_1} \qquad (10.40)$$

Where 'a' is the mean activity which is the same for both ions.

We also know that

$t_a = 1 - t_c$ and $t_a + t_c = 1$

So Eq. (10.40) becomes

$$E_J = -t_c \frac{RT}{F} \ln \frac{a_2}{a_1} + (1 - t_c) \frac{RT}{F} \ln \frac{a_2}{a_1}$$

$$E_J = -2t_c \frac{RT}{F} \ln \frac{a_2}{a_1} + \frac{RT}{F} \ln \frac{a_2}{a_1}$$

$$E_J = (1 - 2t_c) \frac{RT}{F} \ln \frac{a_2}{a_1} \qquad (10.41)$$

From equation (10.41) it follows that the sign of liquid-liquid junction potential is dependent upon the relative values of transference number of cations and anions.

Elimination of Liquid Junction Potential

The introduction of liquid-liquid junction potential interferes with the exact measurement of the potential difference and emf of the cell. It means that an attempt should be made:

(i) to minimize or avoid the liquid-liquid junction potential.

(ii) or the junction may be set up in a reproducible manner and potential is measured.

In order to eliminate the liquid-liquid junction potential, a salt bridge is commonly employed. Salt bridge is a device generally prepared from agar-agar solution containing some salts like KCl, KNO_3 NH_4Cl, NH_4NO_3 etc. The salt is added to agar-agar solution to make it conducting. The salt bridge is interposed between two electrodes of the cell as shown is Fig. 10.8.

The above cell is represented as

$$Zn \mid ZnSO_4(aq) \parallel CuSO_4(aq) \mid Cu$$

Salt bridge

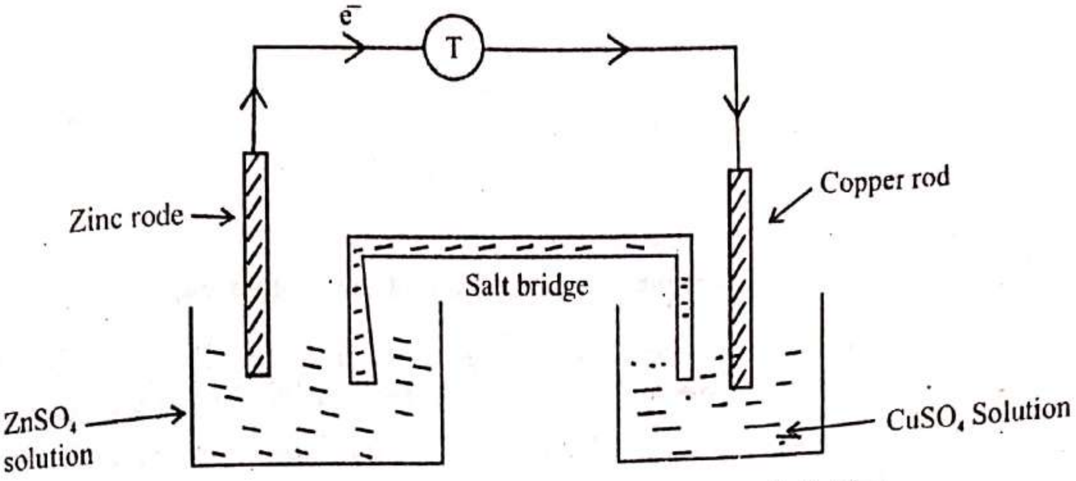


Fig. 10.8. The Daniell cell containing the salt bridge

The salt bridge is supposed to minimize or eliminate the liquid junction potential. Exactly, how this reduction is accomplished is not quite clear, but it is supposed to be associated with the fact that two ions (K^+ and Cl^-) in KCl or (NH_4^+ and NO_3^-) in NH_4NO_3 possess nearly equal speeds and these operate to yield junction potentials between two solutions of the cell and salt bridge. These potentials are opposite in sign and hence cancel each other. It is still more questionable whether there such bridge can reduce the junction potentials to a point where they are negligible, Neverthelees, effective or not, the fact remains that salt bridges have come in to existence.

The second method involves the addition of indifferent electrolytes, at the same concentration to both sides of the cell. If the added substance has a concentration greater than that of any other electrolyte, then the added salt carries almost the whole of the current across the junction between the two solutions. As the concentration of added salt is same on both sides of the boundary then the liquid junction potential will be negligible. This method is not used these days because the indifferent electrolyte added has a marked effect on the activity of the substance in solution.

10.14 CONCEPT OF OVER-POTENTIAL

Deviation from equilibrium potential is called over-potential. It is denoted by η and mathematically may be defined as

$$\eta = E - E_{eq}$$

Where E is the value of potential at any value of current during electrochemical process while Eeq is the value of potential at zero current. Units of over-potential are same as that of potential.

Current over-potential equation

The relation between current and over-potential in an electrochemical system involving mass transfer controlled redox reaction is called current over-potential equation. Mathematically current-over potential equation for the reaction of the type

$$O + ne^- \rightleftharpoons R$$

can be written as:

$$i = \left[\frac{C_o(o,t)}{C_o^*} e^{-\alpha n f \eta} - \frac{C_R(o,t)}{C_R^*} e^{(1-\alpha) n f \eta}\right] \tag{10.42}$$

Where i represents current as a function of over-potential (η). $C_o(o,t)$ is surface concentration of an electroactive specie 'O' at any time 't' while C_o^* is the bulk concentration of electroactive specie 'O' and can be treated as a constant quantity. C_R^* is the bulk concentration of specie 'R' while $C_R(o,t)$ is surface concentration of 'R' at any time 't'. α is transfer co-efficient/ symmetry fsctor. It is dimensionless quantity. Its values range from 0 to 1. The n is number of electrons involved in electrochemical reaction while f is constant equal to $\frac{F}{RT}$ where F is Faraday constant.

Butler-Volmer equation

Under limiting conditions where mass transfer is negligible, current-overpotential equation given in equation (10.42) can be transferred into another equation (10.43) which is known as Butler-Volmer equation. By putting $C_o(o,t) = C_o^*$ and $C_R(o,t) = C_R^*$ in eq. 1, we get

$$i = \left[e^{-\alpha n f \eta} - e^{(1-\alpha) n f \eta}\right] \tag{10.43}$$

Butler-Volmer equation is highly useful mathematical equation in electrochemistry. Special cases of Butler-Volmer equation and their significance has been in the following sections:

(i) When value of η is very small

When value of overpotential is very small then relation between current and over-potential becomes linear. Usually $e^x = 1 + x$ (when x is very small), Butler-Volmer equation can be written as:

$$i = i\left[1 - \alpha n f \eta - \{1 + (1-\alpha) n f \eta\}\right]$$

$$i = i\left[1 - \alpha f \eta - 1 - n f \eta + \alpha n f \eta\right]$$

By simplifying above equation, we get

$$i = i_o(-n f \eta)$$

By re-arranging above equation

$$1 = i_o n f\left(\frac{\eta}{i}\right)$$

The ratio of over-potential to current can be considered as charge transfer resistance R_{ct}.

Hence $1 = i_o nf R_{ct}$

Or $R_{ct} = \frac{1}{i_o nf}$

Since f=F/RT, So

$$R_{ct} = \frac{RT}{i_o nF}$$

The value of charge transfer resistance can be determined by using above equation.

It is kinetic parameter and can be used to estimate the speed of electrochemical reaction

(ii) When value of η is very large and negative

When value of over-potential is very large and negative then relation between i and η does not remain linear but becomes logarithmic. Under such condition, anodic component of the current becomes negligible i.e.

$$e^{-(1-\alpha)nf\eta} = \frac{1}{e^{(1-\alpha)nf\eta}} = \frac{1}{\infty} = \text{zero}$$

Butler-Volmer equation is converted into another equation which is known as Tafel's equation (10.44) as given below

$$i = i_o e^{-\alpha nf\eta}$$

By taking natural logarithm on both sides

$$\ln i = \ln i_o - \alpha nf\eta$$

$$\ln i = \ln i_o - \alpha n\frac{F}{RT}\eta$$

By converting natural logarithmic into common logarithmic, we get

$$2.303\log i = 2.303\log i_o - \alpha n\frac{F}{RT}\eta$$

$$\log i = \log i_o - \alpha n\frac{F}{2.303RT}\eta \qquad (10.44)$$

Equation (10.44) is equation of straight line in intercept form. The value of logi against η can be used for determination of α and i_o. The value of transfer co-efficient can be determined from slope of plot of logi vs η while i_o can be determined from intercept of the same plot.

ii- When value of η is large and positive

Tafel's equation with positive slope of logi vs η plot can be obtained by setting large and positive value of η. Under large and positive value of over-potential, cathodic component of current becomes negligible. i.e

$$e^{-\alpha nf\eta} = \frac{1}{e^{-\alpha nf\eta}} = \frac{1}{\infty} = zero$$

$$\ln i = \ln|i_o| + (1-\alpha)nf\eta$$

$$\ln i = \ln |i_o| + (1-\alpha)n\frac{F}{RT}\eta$$

$$\log i = \log |i_o| + \frac{(1-\alpha)nF}{2.303RT}\eta \qquad (10.45)$$

Equation (10.45) is also an equation of straight line in intercept form. The value of i_o and that of α can be determined from intercept and slope of logi vs η respectively.

Determination of symmetry factor

The value of symmetry factor (α) can be determined using different approximation given in above sections. There are few others which can be used for determination of one of these methods of determination of α. This method does not involve any approximation. Butler-Volmer equation can be re-arranged in the following:

$$i = i_o\left[e^{-\alpha nf\eta} - e^{(1-\alpha)nf\eta}\right]$$

$$i = i_o\left[e^{-\alpha nf\eta} - e^{-\alpha nf\eta}\cdot e^{nf\eta}\right]$$

$$i = i_o e^{-\alpha nf\eta}\left[1 - e^{nf\eta}\right]$$

$$\frac{i}{1-e^{nf\eta}} = i_o e^{-\alpha nf\eta}$$

By taking natural logarithmic on both sides

$$\ln\left(\frac{i}{1-e^{nf\eta}}\right) = \ln i_o + (-\alpha nf\eta)$$

Or $$\log\left(\frac{i}{1-e^{nf\eta}}\right) = \log i_o - \frac{\alpha nf}{2.303RT}\eta \qquad (10.46)$$

Equation (10.46) is called Allen and Hickling equation which is also a straight-line equation. Slope of the plot $\log\left(\frac{i}{1-e^{nf\eta}}\right)$ vs η can be used for determination of α.

10.15 VOLTAMMETRY

Voltammetry is a group of electroanalytical techniques which deals with the interplay between electricity and chemistry, namely, the measurements of electrical quantities, such as current, potential, or charge and their relationship to chemical parameters. Such use of electrical measurements for analytical purposes has found a vast range of applications, including environmental monitoring, industrial quality control, or biomedical analysis. In contrast to many chemical measurements, which involve homogeneous bulk solutions, electrochemical processes take place at the electrode–solution interface. The term voltammetry is derived from electrical parameters/units, *volt-am* (pere)-*metry*. *Voltammetry* may be defined as *"the study of current voltage relation at a micro electrode, called working electrode"*. In other words, the technique is based upon the potential current behavior of a polarizable electrode in the solution being analyzed. According to the recommendation of IUPAC, voltammetry is the general term to be used when the current potential relationships are being investigated. The surface area of voltammetry electrode is very small ($0.0001\ m^2$) which is helpful in providing response of current produced by species in solutions. It is also important to clarify here that when mercury (flowing through a fine capillary seems to be emerging as a droplet) is used as a small electrode in voltammetric cell, the technique has a specific name, *polarography*.

Basic principle of voltammetry

All the electrochemical techniques involve the use of electricity either as an input or output signal. The principle of voltammetry technique is to generate an input electrical signal and to measure corresponding output electrical signal. The input signals can be a preprogrammed function of time whereas the output signals may change with time due to sample under investigation. The signals are typically voltage, current and charge where charge is the integration of current with time. The input electrical signals usually cause the electrochemical reactions at working and counter electrodes. Simply; a measured small potential is established across a pair of electrodes, one of which is a non-polarizable reference electrode and the other a polarizable inert electrode. The current which flows depends upon composition of the solution.

Voltammogram

A plot of current as a function of applied potential is called a Voltammogram. It is the electrochemical equivalent of a spectrum in spectroscopy, providing quantitative and qualitative information about the species involved in the oxidation or reduction reaction

$$O + ne \leftrightarrow R$$

where O and R are the oxidized and reduced forms, respectively, of the redox couple. Such a reaction will occur in a potential region that makes the electron transfer thermodynamically or kinetically favorable. For systems controlled by the laws of thermodynamics, the potential of the electrode can be used to establish the concentration of the electroactive species at the surface [$C_O(0,t)$ and $C_R(0,t)$] according to the Nernst equation. On the negative side of E°, the oxidized form thus tends to be reduced, and the forward reaction (i.e., reduction) is more favorable. The current resulting from a change in oxidation state of the electroactive species is termed the *faradaic current* because it obeys Faraday's law (i.e., the reaction of 1mol of substance involves a change of n × 96,487C). The faradaic current is a direct measure of the rate of the redox reaction.

The pathway of the electrode reaction can be quite complicated, and takes place in a sequence that involves several steps. The rate of such reactions is determined by the slowest step in the sequence. Simple reactions involve only mass transport of the electroactive species to the electrode surface, electron transfer across the interface, and transport of the product back to the bulk solution. More complex reactions include additional chemical and surface processes that either precede or follow the actual electron transfer. The net rate of the reaction, and hence the measured current, may be limited by either mass transport of the reactant or the rate of electron transfer. The more sluggish process will be the rate-determining step. Whether a given reaction is controlled by mass transport or electron transfer is usually determined by the type of compound being measured and by various experimental conditions (electrode material, media, operating potential, mode of mass transport, time scale, etc.).

Cyclic voltammetry

One of the more complex electrochemical techniques, cyclic voltammetry is very frequently used because it offers a wealth of experimental information and insights into both the kinetic and thermodynamic details of many chemical systems. Cyclic voltammetry consists of scanning linearly the potential of a stationary working electrode (in an unstirred solution), using a triangular potential waveform (Figure 10.2). Depending on the information sought, single or multiple cycles can be used. During the potential sweep, the potentiostat measures the current resulting from the applied potential. The resulting current–potential plot is termed a cyclic voltammogram. The cyclic voltammogram is a complicated, time-dependent function of a large number of physical and chemical parameters.

Cyclic voltammetry is often the first experiment performed in an electroanalytical study. In particular, it offers a rapid location of redox potentials of the electroactive species, and convenient evaluation of the effect of media on the redox process. Figure 14.2 illustrates that only the oxidized form O is present initially. Thus, a negative-going potential scan is chosen for the first half-cycle, starting from a value where no reduction occurs.

The characteristic peaks in the cycle voltammogram are caused by the formation of the diffusion layer near the electrode surface. These can be best understood by carefully examining the concentration–distance profiles during the potential scan. The most common experimental configuration for recording cyclic voltammogram consists of an electrochemical cell that has three electrodes, i.e., counter or auxiliary electrode (C), reference electrode (R), and working electrode (W), all immersed in a liquid and connected to a potentiostat. The potentiostat allows the potential difference between the reference and working electrode to be controlled with minimal interference from IR (ohmic) drop. In this configuration, the current flowing through the reference electrode also can be minimized thereby avoiding polarization of the reference electrode and hence keeping the applied potential distribution between the working and reference electrode stable. Positioning the reference electrode close to the working electrode further helps to minimize the IR drop between the reference and working electrode due to the resistivity of the solution phase.

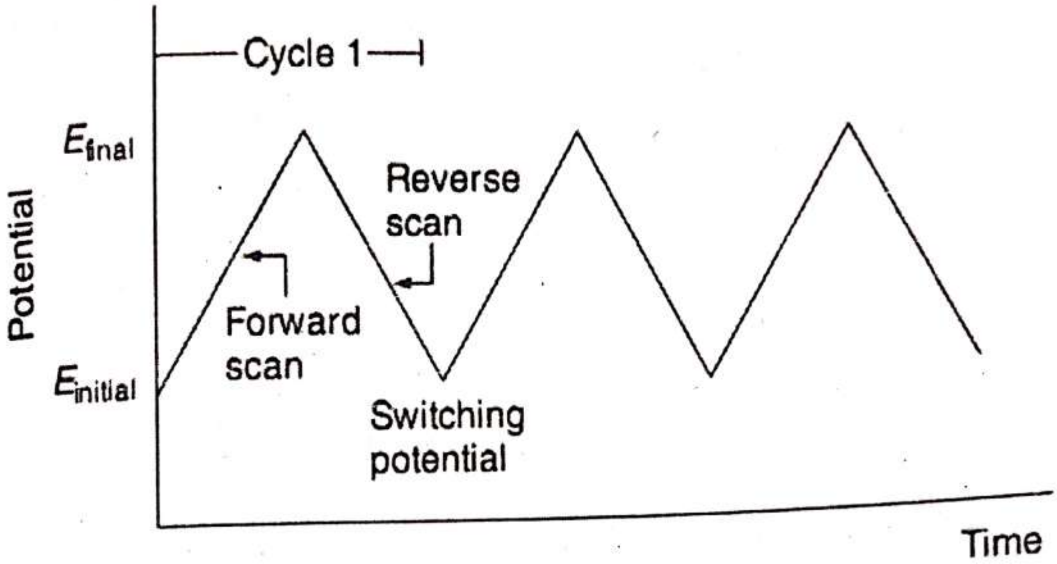


Figure 10. 9. Potential–time excitation signal in a cyclic voltammetric experiment.

Reference electrode: Commonly used are aqueous Ag/AgCl or calomel half cells, which can be obtained commercially or easily prepared in the laboratory.

Counter electrode: Non-reactive high surface area electrode, commonly platinum gauze.

Working electrode: Most commonly used are inlaid disc electrodes (Pt, Au, graphite, glassy carbon, etc.) of well-defined area. Other geometries may be employed beneficially in appropriate circumstances (dropping or hanging mercury hemisphere, cylinder, band, arrays, or grid electrodes).

Data Interpretation

The cyclic voltammogram is characterized by several important parameters. Four of these observables, the two peak currents and two peak potentials, provide the basis for the diagnostics developed by Nicholson and Shain for analyzing the cyclic voltammetric response.

Stripping voltammetry

Stripping voltammetry is an extremely sensitive electrochemical technique for measuring trace metals. Its remarkable sensitivity is attributed to the combination of an effective pre-concentration step with advanced measurement procedures that generate an extremely favorable signal background ratio. Since the metals are pre-concentrated into the electrode by factors of 100–1000, detection limits are lowered by two to three orders of magnitude compared to solution-phase voltammetric measurements. Hence, four to six metals can be measured simultaneously in various matrices at concentration levels down to 10–10 M, utilizing relatively inexpensive instrumentation. The ability to obtain such low detection limits strongly depends on the degree to which contamination can be minimized. Expertise in ultra-trace chemistry is required.

Essentially, stripping analysis is a two-step technique. The first, or *deposition step*, involves the electrolytic deposition of a small portion of the metal ions in solution into the mercury electrode to pre-concentrate the metals. This is followed by the *stripping step* (the measurement step), which involves the dissolution (stripping) of the deposit. Different versions of stripping analysis can be employed, depending on the nature of the deposition and measurement steps.

10.16. FUEL CELLS

Fuel cells are the electrochemical devices in which chemical energy of the fuel is directly converted into electrical energy.

or

Fuel cells are the electrochemical devices which convert the energy of fuel oxidation reactions into electrical energy.

Theoretically the effectiveness of transforming chemical energy into electrical energy through heat is very slow. For this reason, at the end of 19th century, scientists attempted to create devices for the direct conversion of chemical energy into electrical energy without the intervention of thermal devices such as generators turbines etc. This required the development of galvanic cells in which the reactions of oxidation of the fuel and reduction of the oxygen proceed electrochemically. The first fuel cell was constructed in 1839 by the British physicist and lawyer Sir William Robert Grove; it had platinum electrodes with hydrogen bubbled over one electrode and oxygen over the other. For many years little was done to develop fuel cells for commercial purposes, but since the 1960s there has been a considerable revival of interest in this problem, particularly in view of present energy shortages. Recent advances in technology and electrochemistry have made the scientists successful to introduce the fuel cell which are more efficient, than thermal source of electrical energy. Fuel cells have been used as sources of auxiliary power in space craft, and major research efforts are under-way to develop their use in automobiles in order to minimize air pollution and noise Fuel cells employ the same electrochemical principles as conventional cells. Their distinguishing feature is that the reacting substances are continuously fed into the system, so, that fuel cells, unlike conventional cells, do not have to be discarded when the chemical are consumed. In fuel cells an attempt is made to make the fullest possible use of the free energy of reactions, such as combustion of fuels, to produce electrical energy. Processes are chosen which occur as nearly reversible as possible in order to obtain the maximum useful proportion of free energy change. The mode of operation of fuel cells is fundamentally different from that of batteries. While batteries store electrical energy fuel cells convert energy obtainable from chemical powers directly into electrical energy.

Kinds of Fuel Cells

Depending on the kind of fuel used, we have the following types of fuel cells:

(i) Hydrogen-oxygen fuel cell.
(ii) Hydrocarbon-oxygen fuel cell
(iii) Carbon monoxide-oxygen fuel cell
(iv) Methyl alcohol-oxygen fuel cell
(v) Solid coal-oxygen fuel cell

Hydrogen-Oxygen Fuel Cell

This fuel cell consists of two electrodes made of porous graphite. Platinum is coated on the surface of the electrodes. The electrodes are placed in aqueous solution of NaOH or KOH. Hydrogen and oxygen are bubbled into the cell under a pressure of about 50 atm. When the electrodes are connected, a flow of electric current takes place.

The electrode reactions are:

Anode reaction:

$$H_2 \longrightarrow 2H^+ + 2e^-$$

$$2H^+ + 2OH^- \longrightarrow 2H_2O$$

The net half-cell reaction is

$$H_2 + 2OH^- \longrightarrow 2H_2O + 2e^-$$

Cathode reaction:

$$\frac{1}{2}O_2 + H_2O + 2e^- \longrightarrow 2OH^-$$

Now, the overall cell reaction is

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$$

The emf of the cell is found to be 1.23 volts. The cell reaction is the same as combustion of H_2 in air or oxygen. The energy of the fuel oxidation has not been liberated as heat but it has being directly converted into electrical energy. Fig. 10.9 gives a schematic diagram of such cell.

For an efficient cell all processes must occur rapidly. Reactant must be able to reach the electrodes easily so that porous electrodes with large internal surface area, saturated with electrolyte, are used. Such cells are used in space crafts. The electrolyte used in these cells is an ion-exchange material and not a solution of NaOH or KOH. This ion-exchange material is used in the form of a membrane. This membrane allows easy flow of protons (H^+) which react with O_2 and electrons to form H_2O.

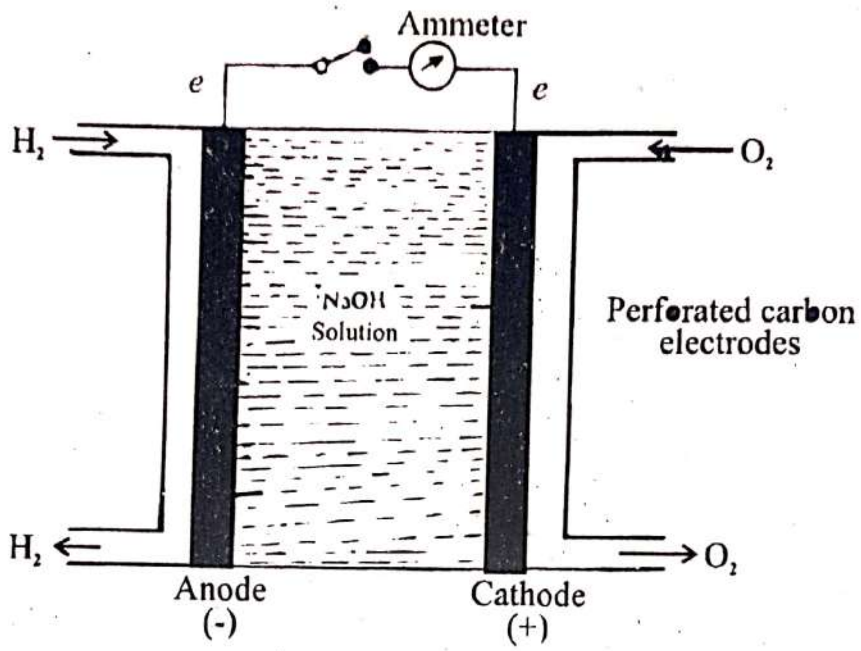


Fig. 10.9 Hydrogen-Oxygen Fuel Cell.

Efficiency of Fuel Cells

The ability of a cell to convert chemical energy of a fuel-oxidation reaction into electrical energy is expressed in terms of efficiency of the cell (ε). It is defined as

$$\varepsilon = \frac{\Delta F}{\Delta H} \times 100 \tag{10.42}$$

Where ΔH = Maximum available heat, when oxidation of fuel Occurs at constant temperature and pressure.

ΔF = The part of this energy i.e., part of ΔH, convertible into electrical energy

The efficiency of different fuel cells is given as under:-

1. $H_2 - O_2$ fuel cell: $\Delta F^o = -273.2$ kJ mole^{-1}

$\Delta H^o = -258.9$ kJ mole^{-1}

$$\therefore \quad \epsilon = \frac{\Delta F}{\Delta H} = \frac{-273.2 \times 100}{-258.9} = 83\%$$

2. Carbon O_2 fuel cell: $\epsilon = \frac{\Delta F}{\Delta H} = \frac{-137.3 \times 100}{-110.0} = 124\%$

3. CH_4-O_2 fuel cell: $\epsilon = \frac{\Delta F}{\Delta H} = \frac{-818.0 \text{kJ mole}^{-1} \times 100}{-890.4 \text{kJ mole}^{-1}}$

$= 92\%$

4. CH_3OH-O_2 fuel cell: $\epsilon = \frac{\Delta F}{\Delta H} = \frac{-706.9 \text{ kJ mole}^{-1} \times 100}{-764.0 \text{kJ mole}^{-1}} = 93\%$

Superiority of Fuel Cells

1. The fuel cells possess very high efficiency. By using certain kinds of fuel in such cells 75-90 percent conversion of chemical energy of the fuel into electrical energy has been made possible. In heat engines the efficiency does not exceed 40 percent.
2. The individual cells can be stacked and connected in series to generate higher voltage.
3. They are also very light.
4. The fuel cells do not create pollution problems.
5. These cells play an important role in manned space flights.

Practical Success of Fuel Cells

Owing to various technological and operational difficulties (such as increased requirements of the purity of the fuel, the insufficient period of services, etc.), however the economical advantages of the fuel cells even with their higher efficiency are still not clear. For this reason, the possibility of using them for production of electrical energy, instead of heat power plants, requires further study. If these problems could be solved, the fuel cell technology would bring revolution in the area of energy production. There is no doubt, however that for more limited purposes fuel cells will find broad applications in the nearest future (e.g., they have been successfully employed in the manned space flights.)

10.17. CORROSION AND ITS PREVENTION

The process of eating away of a metal as a result of electrochemical reaction is Called corrosion. It is the formation of metal oxides by an electrochemical reaction is called corrosion.

Types of corrosion

Corrosion can be classified into atmospheric corrosion (Rusting), Immersed corrosion (In water) and underground (In pipes) depending upon place of corrosion. Corrosion is generally occurred in the presence of followings of an electrolyte, electrodes (Cathode and Anode) and an oxidant.

Theories of Corrosion

There are different theories which explain in the process of corrosion acid theory and electrochemical theory are common theories of corrosion. Electrochemical theory of corrosion has been described here. According to this theory, corrosion is a result of an electrochemical reaction during corrosion process an electrochemical cell is formed and a redox reaction occurs within cell as explained below.

The process of rusting of iron can be used to explain mechanism of corrosion according to electrochemical theory. Water droplet present iron metal can be treated as an electrochemical cell in which iron acts as anode and impurity acts as cathode. Following reactions occurs in this cell.

Reaction at anode: (Iron)

Oxidation takes place at this electrode;

$$Fe \rightarrow Fe^{2+} + 2e^-$$

$$2Fe \rightarrow 2Fe^{2+} + 4e^-$$

Reaction at cathode: (Impurity)

Reduction takes place at this electrode;

$$2H_2O + O_2 + 4e^- \rightarrow 4OH^-$$

Overall Reaction:

$$2Fe + 2H_2O + O_2 \rightarrow \underset{\text{(Solid)}}{2Fe(OH)_2}$$

$$2Fe(OH)_2 + O_2 \rightarrow 2Fe_2O_3.H_2O + 2H_2O$$

Following methods are used to prevent corrosion.

Coating

Corrosion can be prevented by coating the material with corrosion resisting material like Noble metals , Polymeric material(Grafting) and painting etc.

Alloy formation

Corrosion can also prevent by mixing two metal homogeneously.

Painting

Painting is also applied to prevent corrosion.

QUESTIONS

Q.1. (a) What are electrochemical cells? Discuss the significance of electrochemical cells in daily life and industry.

(b) Explain the difference between electrolytic and galvanic cells with suitable examples.

Q.2. (a) Write a short note on Daniell cell.

(b) Explain the difference between chemical and concentration cell.

Q.3. (a) What do you understand by half-cell reactions? Explain such types of reactions with suitable examples.

(b) What are reversible and irreversible cells? Elaborate your answer with suitable examples.

Q.4. (a) Discuss the significance of electrodes in electrochemistry.

(b) Explain various types of reversible electrodes.

Q.5. (a) What do you understand by electromotive force (emf) of a cell? How is it measured experimentally?

(b) What is electrode potential? Explain oxidation and reduction potentials.

(c) Briefly explain Nernst theory of electrode potential.

Q.6. (a) Explain the standard hydrogen electrode.

(b) How is the electrode potential determined?

Q.7. (a) What is standard cell potential? How is it determined?

(b) A galvanic cell was constructed using electrodes of Pb and PbO_2 with H_2SO_4 as electrolyte. The half-cell reactions and reduction potentials in the system are:

$$PbO_2(s) + 4H^+ + SO_4^{2-}(aq) + 2e^- \rightleftharpoons PbSO_4(s) + 2H_2O \qquad E^0_{PbO_2} = 1.69V$$

$$PbSO_4(s) + 2e^- \rightleftharpoons Pb(s) + SO_4^{2-}(aq) \qquad E^0_{PbSO_4} = -0.36V$$

What is the cell reaction and what is the standard potential of the cell?

Ans. $PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e^- \longrightarrow PbSO_4(s) + 2H_2O$ reduction

$Pb(s) + SO_4^{2-}(aq) \longrightarrow PbSO_4(s) + 2e^-$ oxidation

Net reaction $PbO_2(s) + 4H^+(aq) + Pb(s) + Pb(s) + 2SO_4^{2-}(aq) \longrightarrow 2PbSO_4 + 2H_2O$

$E^0_{cell} = 2.05V$

Q.8. (a) Derive the relationship between free energy and cell potential. How would you predict the feasibility of a reaction from cell potential measurements.

(b) What spontaneous reaction will occur if Cl_2 and Br_2 are added to a solution containing Cl^- and Br^-? (Ans. $Cl_2 + 2Br \longrightarrow Br_2 + 2Cl^-$)

(c) Using the Table 10.2, predict the reaction that will occur when Ni and Fe are added to a solution containing both Ni^{2+} and Fe^{2+} ions. (Ans. $Ni^{2+}(aq) + Fe(s) \longrightarrow Ni(s) + Fe^{2+}(aq)$)

Q.9. (a) Is it possible to measure the emf of an isolated cell? Explain your answer.

(b) What do the positive and negative signs of reduction potentials tell us?

(c) What is a galvanic cell? What is a half-cell.

Q.10. (a) What is standard cell potential? How do the ΔS and ΔH are calculated from standard cell potential?

(b) How is equilibrium constant determined from cell potential?

(c) From the position of half-cell reaction in table 10.2, determine whether the following reactions are spontaneous.

(i) $3Fe^{2+} + 2NO + 4H_2O \longrightarrow 3Fe + 2NO_3 + 8H^+$

(ii) $3Ca + 2Cr^{3+} \longrightarrow 2Cr + 3Ca^{2+}$

(iii) $Br_2 + 2Cl^- \longrightarrow Cl_2 + Br^-$

(iv) $Ni^{2+} + Fe \longrightarrow Fe^{2+} + Ni$

(d) Using the data in table 10.2, calculate cell potential of the reaction.

$Cd^{2+} + Fe \longrightarrow Cd + Fe^{2+}$

Q.11. (a) Explain thermodynamics of single electrode potential.

(b) Explain the effect of concentration of electrode potential.

(c) What is Nernst equation? Discuss its significance.

(d) What is the equation that relates the equilibrium constant to the standard cell potential.

Q.12. (a) The following reaction

$2AgI + Sn \rightleftharpoons Sn^{2+} + 2Ag + 2I^-$,

has a standard cell potential –0.015V. What is the value of Kc for this reaction.

(b) Calculate the AF° for the following reaction as written

$2Br^- + I_2 \longrightarrow 2I^- + Br_2$

(c) Calculate Kc for the system, $Ni^{2+} + Co \rightleftharpoons Ni + Co^{2+}$ using the data in table 10.2.

Q.13. (a) What are electrochemical cells? Explain the difference between electrolytic and galvanic cell with suitable examples.

(b) What are electrode concentration cells? How would you determine the emf of cells with amalgam electrodes?

(c) Determine the emf of electrode concentration cell with gaseous electrodes.

Q.14. (a) What are electrolyte concentration cells? How would you calculate the emf of concentration cells with and without liquid junction.

(b) Write a detailed note on concentration cells with transport.

Q.15. (a) What is liquid junction potential? How is produced?

(b) How liquid junction potential of a cell is determined?

(c) How is liquid junction potential eliminated.

Q.16. What is salt bridge? Explain its significance in electrochemical cells.

Q.17. (a) What are fuel cells? Explain the working principle of a fuel cell.

(b) How is the efficiency of a fuel cell determined?

(c) Discuss future prospectus of fuel cells.

Q.18. Justify/comment on the following statements.

(i) Galvanic cells produce electrical energy

(ii) Electrolytic cells utilize electrical energy

(iii) Galvanic cell is a reversible cell.

(iv) For reactive metals amalgam electrodes are used.

(v) Redox potential of standard hydrogen electrode is 0.00V.

(vi) Oxidation potential is a measure of tendency to gain electron.

(vii) If osmotic pressure is greater than the solution pressure then metal ionizes.

(viii) Cell potential is used to determine feasibility of a reaction.

(ix) Cell potential is used to determine equilibrium constant of a reaction.

(x) Salt bridge is used to eliminate liquid junction potential.

REFERENCES

1. Glasstone, S. 1995. Physical Chemistry, Macmillan and Co. Ltd. St. Marling Street, London.
2. Maron, S. H. and C. F. Prutton, 2000. Principles of Physical Chemistry, 4th Edition, The Macmillan Company collier-Macmillan Limited, London.
3. Kundu S. and S.K. Jain. Physical Chemistry, S. Chand and Co (Pvt) Ltd, India.
4. Atkins, P.W. 2005. Physical Chemistry, Freeman and Company, New York.
5. Silbey, R. J. Alberty, R. A. and M. G. Bawendi 2005. Physical chemistry, Wiley, India.
6. Barrow, G.M. 1995. Introduction to Molecular Spectroscopy, McGraw-Hill, New York.
7. Fried, V.B. and H.F Hameka. 2004. Physical Chemistry, Macmillan Publishing Company, New York.
8. Laidler, K.J. and J.H. Meiser. 2000. Physical Chemistry, Longman publishers New Delhi India.
9. Glasstone, S. 1997. An Introduction to Electrochemistry, Affiliated East-West press pvt. Limite New Delhi.
10. Castellan, G.W. 2001. Physical Chemistry. Narosa Publishing House, New, Delhi.
11. Ball, D.W. 2000. Physical Chemistry, Thomson books/ U.K.
12. Simon J.D. and D.A. McQuarrie. 2001. Physical Chemistry, Viva Book Private limited New Delhi.

Chapter 11

EMULSIONS AND GELS

11.1 INTRODUCTION

This chapter deals with the chemistry of non-homogenous two phase system, i.e. gels and emulsions. Dispersed phase is liquid in both gels and emulsions. While, dispersion medium is liquid in emulsions and solid in gels. Research about preparation methods and nature of these systems is a current research area in the world of science.

Emulsions are liquid in liquid colloidal system. The size of droplets of dispersed phase, appearance and outlook of emulsion, type of emulsifier and physical state of dispersion medium are some tools which are used in this chapter to classify the emulsions. These multiple classification schemes are possible due to comprehensive information about characterization of emulsions. Techniques like magnetic resonance imaging, dynamic light scattering, fluorescence method and conductivity help to determine type of emulsions. Type of emulsion means to configure the nature of dispersed as well as dispersion medium. Sedimentation and ultracentrifugation methods are used to determine the size of droplets of dispersed phase. Stable emulsion cannot be successfully prepared without emulsifier. Concentration of this complementary component of emulsion is very important for a stable emulsion. Critical micelle concentration is that concentration of emulsifier at which micellization starts. Many methods like conductometry, solubility measurement and surface tensiometry which can help to determine critical micelle concentration have been discussed in this chapter. Factors related to micellization are also covered in this chapter along with thermodynamic study of micellization. Emulsion formation process is also governed by qualitative and quantitative theories which also determine factors related to stability of emulsions. Comprehensive discussion about stability and demulsification is also written here. Advanced and conventional preparative methods of emulsions and current applications of emulsions are also discussed here. In this way we tried to cover all aspects of emulsions to convey multidimensional study about emulsions to readers.

The scope of present chapter deals with another colloidal system named gels. Gels have liquid as inner phase and solid as outer phase. Systematic and multiple classification of gels has been discussed in this chapter on basis of nature of dispersion medium, dispersed phase, crosslinkage and sensitivity of gels. Structure of gels and different preparation methods of gels are also written in this chapter. Thixotropy, swelling, deswelling and responsive properties of gels are also explained here. Application of gels in drug delievery, glucose sensitivity, catalysis, coating industry and nanotechnology is also written here. Thus scope of current chapter is a thorough study about gels and emulsions. All the discussion of this chapter has explained on logical scientific basis along with suitable examples and pictorial diagrams.

11.2 SURFACE TENSION

Surface tension is one of the most important properties of liquid. It plays a crucial role in stability of colloidal system especially in emulsification. Therefore in this section we will briefly describe the basic idea of surface tension and interfacial tension.

The molecules of liquid present in bulk are attracted from all sides equally by other molecules of same liquid while molecules at interface are attracted right, left and down ward only. Forces acting left and right ward cancel the effect of each other. There is no significant force acting on surface of molecule vertically upward. Therefore a net force acts vertically downward which causes a tension in surface. This net force acting per unit length is called surface tension of liquid. The surface tension can be defined as "the force in Newton acting at right angle along the surface of a liquid one meter in length". It is generally represented by 'γ'. Its SI units are N/m. Alternatively it is the work done per unit increase of surface area. Mathematically it can be written as

$$dW \propto dA$$

$$dW = \gamma dA \qquad (11.1)$$

Where dW is work, dA is the increase in surface area and proportionality constant 'γ' is surface tension. By rearranging equation (11.1), we get

$$\gamma = \frac{dW}{dA} \qquad (11.2)$$

Equation (11.2) can be used to find the units of γ which are Jm^{-2} same as Nm^{-1}.

At constant temperature and pressure the work of increasing the surface area contributes to the differential Gibbs free energy Thus we can write equation (11.1) as

$$dG = \gamma dA \qquad (11.3)$$

Term interfacial tension instead of surface tension is generally used for the interface of two liquids.

Measurement of Surface Tension

There are two different methods for determination of surface tension of liquid. Mostly the capillary rise method and the drop weight method are used. Here we will discuss the capillary rise method.

Capillary Rise Method

This method is based on the fact that any liquid which wets the walls of the glass capillary tube will rise in the tube when the tube is inserted in bulk liquid. While the liquid which does not wet the wall of glass tube shows depression of level of liquid in capillary. The rise or fall of liquid in capillary tube inserted in bulk liquid is due to surface tension.

Consider a capillary tube of radius 'r' immersed in a vessel containing a liquid which wets the glass wall. Due to force of surface tension, liquid level will rise in the capillary tube. The liquid keeps rising upto a certain level of height 'h'. There are two forces which act on liquid in capillary tube. The force due to surface tension acts along the circumference and it can be given as

$$\text{Force due to surface tension} = \gamma(2\pi r)$$

Since force due to surface tension is acting at an angle 'θ' known as contact angle, the upward force. Therefore force acting vertically upward can be written as

$$F_1 = 2\pi r\gamma\cos\theta \tag{11.4}$$

Force acting vertically downward is weight of the liquid and it can be written as

$$F_2 = mg \tag{11.5}$$

We know that density of liquid is defined as

$$\rho = \frac{m}{V}$$

$$m = \rho V$$

$$m = \rho(\text{surface area} \times \text{height})$$

$$m = \rho(\pi r^2 h) \tag{11.6}$$

By putting the value of m from equation (11.6) into (11.5), we get

$$F_2 = \rho(\pi r^2 h)g \tag{11.7}$$

At equilibrium F_1 and F_2 becomes equal to each other. Hence

$$F_1 = F_2$$

$$2\pi r\gamma\cos\theta = \rho(\pi r^2 h)g$$

$$2\gamma\cos\theta = \rho(rh)g$$

$$\gamma = \frac{\rho rhg}{2\cos\theta} \tag{11.8}$$

Where ρ is density of liquid, θ is contact angle, r is radius of capillary tube, g is acceleration due to gravity and h is height of liquid in capillary from the surface of bulk liquid.

When θ is equal to 0° then above expression can be written as

$$\gamma = \frac{\rho rhg}{2}$$

By knowing the values of ρ, r, h and g, surface tension of a liquid can be calculated.

11.3 INTERFACIAL TENSION AND SPREADING OF LIQUIDS

The existence of a surface means a separation between two media, e.g. liquid and gas. In such cases, the surface tension depends upon the nature of both the media in contact. In common practice, the surface tensions of the liquids correspond to those for the interface between the liquid and the air saturated with its vapour. Quite obvious, if the composition of the vapour phase above the liquid is changed, there would be a corresponding change in γ values. Similar considerations apply to the interface between two immiscible or partially miscible liquids. And there is an imbalance of intermolecular forces, the extent of which depends upon the nature of the two liquids. The surface tension values, then are called the interfacial tension. It means that an interfacial tension exists at the boundary between two layers, when two immiscible or partially miscible liquids are brought into contact.

The interface between two mutually saturated immiscible liquids contracts because of the interfacial tension. In principle, the interfacial tension can be measured by all the methods used to measure surface tension but, since interfacial tensions are even more sensitive to impurities than surface tensions, reproducible results can only be obtained with substances that can be highly purified. The magnitude or value of surface tension between two liquids is generally intermediate between the surface tensions of the two liquids, γ_A and γ_B, but sometimes it is lower than both as may be seen from data given below.

Table 11.1 Interfacial tensions of the liquids at 20 °C (dynes/cm)

A	B	γ_A	γ_B	γ_{AB}
Water	Benzene	72.75	28.88	35.00
Water	Carbon tetrachloride	72.75	26.8	45.0
Water	n-Hexane	72.75	18.4	51.1
Water	Mercury	72.75	470.0	375.0
Water	n-Octyl alcohol	72.75	27.5	8.5
Water	Ethyl ether	72.75	17.0	10.7

The work required to enlarge the surface of separation between two immiscible or partially immiscible liquids is called interfacial surface energy, and is often expressed as the interfacial tension in dynes per cm. The interfacial tension between two liquids is generally less than the larger of two surface tensions; mutual attraction across the interface between the molecules of one liquid and those of the other tends to reduce the inward pull of the molecules in the surface by those of its own kind.

If a column of pure liquid 1 cm² in cross-section is pulled apart so that the liquid is divided into two parts, without any lateral contraction, then two new (liquid-gas) surfaces each of 1 cm² area will be formed. Since surface tension is also the work necessary to create unit surface area, the work done in putting the liquid apart is then

$$W_C = 2\gamma \tag{11.9}$$

Two unit surfaces are created. Since the work is done against the forces of cohesion, it is called the work of cohesion of the liquid. In a like manner, if we consider a column composed of two immiscible/partially miscible liquids, then the work required to separate the one liquid from the other against the acting interfacial tension is given by

$$W_a = \gamma_A + \gamma_B - \gamma_{AB} \qquad (11.10)$$

This resultant work is also a measure of the energy required to separate the solid from the liquid and is called the work of cohesion. The equation (11.10) is a form of the equation first deduced by A. Dupre (1869) and generally known by his name.

Spreading of One Liquid from One Another

If a liquid A to spread spontaneously on another liquid B, in which it does not dissolve, the process must be accompanied by a decrease of free energy. In the spreading, the interfaces between A and B and that between A and its vapour are increased, whereas that between B and its vapour is decreased and so far spontaneously it follows that $\gamma_A + \gamma_B - \gamma_{AB}$ must be negative, i.e.

$$\text{Net work done in spreading } 1\ \text{cm}^2 = \gamma_A + \gamma_B - \gamma_{AB} < 0 \qquad (11.11)$$

(Decease in free energy = Useful work =– ive sign)

Where γ_A and γ_B are the surface tensions of A and B respectively against their vapours and γ_{AB} is the interfacial tension between two liquids. The form of Dupre's equation for the adhesional work between A and B is

$$W_{AB} = \gamma_A + \gamma_B - \gamma_{AB} \qquad (11.12)$$

Where W_{AB} is a measure of the work required to diminish the surface between A and B by 1 cm_2, the surfaces of A and vapour, and of B and vapour increasing by this amount at the same time, combination of equations (11.11) and (11.12) shows that the condition for spreading is

$$W_{AB} > 2\gamma_A \qquad (11.13)$$

That is to say, that the work of adhesion (W_{AB}) between A and B must exceed the work of cohesion ($2\gamma_A$) of the spreading liquid A. The difference between these two quantities, i.e.,

$$W_a - W_{CA} = \gamma_A + \gamma_B - \gamma_{AB} - 2\gamma_A$$

$$S_{AB} = \gamma_B - \gamma_A - \gamma_{AB}$$

S_{AB} is called the spreading coefficient of A on B. If the liquid B is to spread on the surface of A, then

$$S_{BA} = W_a - W_{CB}$$

$$S_{BA} = \gamma_A + \gamma_B - \gamma_{AB} - 2\gamma_B$$

$$S_{BA} = \gamma_A - \gamma_B - \gamma_{AB}$$

S_{BA} is the spreading coefficient of B on A (W. D. Harkins 1922).

A positive value of S_{AB}/S_{BA} indicates that when a small quantity of liquid A is placed on the surface of B, it will spread across the surface like oil on water. On the other hand when S_{AB} is negative, no spreading will take place and the added liquid will remain as a drop on the surface.

As a result of comprehensive study of surface tensions of organic compounds W. D. Harkins observed that spontaneous having a polar group of type, –OH, –COOH, –CN or $-NH_2$ were able to spread on water whereas the hydrocarbon and halogen derivatives did not spread; some of the relevant data are given below.

Table 11.2 Spreading of liquids on water (dynes/cm units)
[substance B is water]

Substance A	γ_A	γ_B	γ_{AB}	S_{AB}
Octyl alcohol	27.5	72.5	8.5	36.5
Oleic acid	32.5	72.5	15.5	24.5
Bromoform	41.5	72.5	40.8	–9.8
Liquid paraffin	31.8	72.5	57.2	–16.5

Anton off's Rule

In developing the conditions for one liquid to spread on another, it was assumed that the liquids are not mutually soluble, so that their surface tensions remain unchanged; when each liquid dissolves in the other, the tensions are altered, and G. N. Anton off (1907) suggested the rule that when two saturated liquid layers are in equilibrium, the tensions at the interface between two liquids is equal to the difference of the two surface tension values. The interfacial tension γ_{AB} is less than the layer of two values.

$$\gamma_{AB} = \gamma_A - \gamma_B \text{ or } \gamma_B - \gamma_A \qquad (11.14)$$

It follows, according to the Anton off's rule that when two partially miscible liquids are in equilibrium, the spreading coefficient $\gamma_B - \gamma_A - \gamma_{AB}$ is zero. The rule generally applies quite accurately for liquids having positive "initial" spreading coefficients; (when one tends to spread on the other in pure state); if the coefficient for the pure state is negative, the interfacial tension is generally greater than the value given by v. It is probable that the difference in the behavior is due to the fact that the contact angle between two liquids at equilibrium is almost zero for systems of former type, but not for the latter. It is only for zero contact angles that $\gamma_B - \gamma_A - \gamma_{AB}$ is the strict measure of the spreading tendency. The interfacial tensions play a vital role in the properties of the emulsions and the detergents.

Interfacial Tension

When two immiscible or partially miscible liquids A and B are contacted, it is found that an interfacial tension exists at the boundary between two layers. It is denoted by γ_{AB}.

or

The surface tension existing at the interface of two partially or completely miscible liquids is called interfacial tension.

11.4 PRESSURE DROP ACROSS A CURVED SURFACE OR CURVED INTERFACES

When we think about the study of different interfaces, we find that the liquid-liquid or liquid-air interfaces are convenient to study because the molecules in the fluid are not rigidly fixed. Therefore they tend to adjust themselves to the changes at the interfaces. A curved surface of a liquid or a curved interface between phases exerts a pressure so that the pressure is higher in the phase on the concave side of the interface than on the convex side. This is analogous to the fact that the pressure inside of a rubber balloon is higher than the atmosphere pressure, because of the pressure exerted by the tension of the rubber. However the difference between the sheet of a rubber and the surface of a pure substance is that the tension of the sheet of rubber is roughly proportional to the distance stretched, but the surface tension of the pure substance is independent of area.

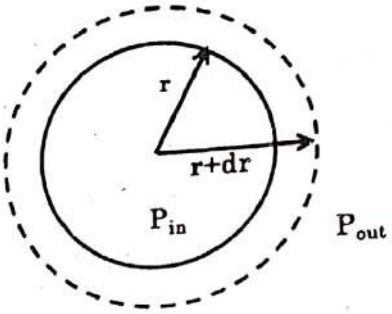


Fig. 11.1 Spherical bubble in a liquid

To derive the relation between the various curvatures of a surface, the pressure difference and the surface tension, we will consider a spherical vapour bubble of various "r" in a liquid at pressure P as illustrated in Fig. 11.1.

$$\gamma = \frac{F}{\ell}$$

$$\text{Surface Gibb's energy} = \frac{\text{Work done}}{\text{Change in surface area}}$$

$$\text{Surface energy} = dG = \gamma \cdot dA$$

$$\left(\frac{\partial G}{\partial A}\right)_{T,P} = \frac{dG}{dA} = \gamma$$

$$A = 4\pi r^2$$

The surface Gibbs energy of the bubble is $4\pi r^2 \times \gamma$. The surface tension is expected to be a function of radius, but the nature of dependence is not known. Therefore we will assume that the surface tension is independent is radius of curvature in the calculations made here. If the radius were to increase by dr, the surface area would increase by $8\pi r \cdot dr$. The surface energy of the bubble would in increase by $8\pi r\, \gamma\, dr$.

$$dG = \gamma \cdot dA$$

$$dG = \gamma[4\pi(r + dr)^2 - 4\pi r^2]$$

$$dG = 4\pi\gamma[r^2 + 2r \cdot dr + (dr)^2 - r^2]$$

$$dG = 8\pi r \cdot \gamma \cdot dr$$

or

$$A = 4\pi r^2$$

$$\frac{dA}{dr} = 4\pi(2r)$$

$$\frac{dA}{dr} = 8\pi r$$

$$dA = 8\pi r \cdot dr$$

dr is small so its square is very small and neglected.

In order for this to happen, the pressure difference ΔP i.e. ($P_{in} - P_{out} = \Delta P$ across the surface would have to increase so that the work against this pressure difference would be equal to the increase in surface energy).

PV work of expansion = Increase in free surface energy

$$4\pi r^2 \cdot dr\Delta P = 8\pi r \cdot \gamma \cdot dr$$

$$\Delta P = \frac{8\pi r \cdot \gamma \cdot dr}{4\pi r^2 \cdot dr}$$

$$\Delta P = \frac{2\gamma}{r} \tag{11.15}$$

and

$$\Delta P = \text{area} \times \text{length}$$

$$\Delta P = 4\pi r^2 \cdot dr$$

Since the radius of curvature in this case is positive, the pressure is greater on the concave side of the interface. As the radius increases to infinity, the difference in pressure approaches zero ($\Delta P \approx 0$), as it must for a planar surface. The pressure drop across a curved surface is responsible for the rise or depression, of a liquid surface in a capillary. Equation (11.15) holds not only for a sphere, but for any surface forming a part of the sphere.

The differential of reversible work dW_{rev} for a process involving a change in volume and change in surface area of the plane surface is given by

$$dW_{rev} = -PdV + \gamma dA$$

11.5 VAPOUR PRESSURE ALONG CURVED SURFACE : KELVIN EQUATION

Due to existence of surface tension, vapour pressure around curved surface is different from that of plane surface of liquid. It has been observed that the vapour pressure of a spherical droplet of a liquid is larger than that of the bulk liquid. This matter was considered by William Thomson and Lord Kelvin. The mathematical expression which relates the surface tension of liquid to vapour pressure of droplets of liquid is known as Kelvin equation. Suppose that the ordinary vapour pressure of a liquid is P_0 and P is the vapour pressure when the liquid is present in the form of droplets of radius r. The change in Gibbs free energy when dn moles of a liquid are transformed from a plane surface to a droplet is given by

$$dG = RT\ln\frac{P}{P_o}dn \tag{11.16}$$

The value of dG can be calculated from surface tension and increase in surface area measurements using equation

$$dG = \gamma dA \tag{11.3}$$

The increase in surface area dA of droplet is

$$dA = 4\pi(r + dr)^2 - 4\pi r^2$$

$$dA = 4\pi[r^2 + 2r \cdot dr + (dr)^2 - r^2]$$

Since r is negligible therefore dr^2 is neglected. Hence

$$dA = 8\pi r \cdot dr \tag{11.17}$$

The value of dr can be calculated as

$$\text{Volume of 1 mol of liquid} = \frac{M}{\rho}$$

$$\text{Volume of dn moles of liquid} = \frac{M}{\rho}dn = 4\pi r^2 dr$$

$$dr = \frac{M}{4\pi r^2 \rho}dn \tag{11.18}$$

By putting the value of dr in equation (11.17) from equation (11.18), we get

$$dA = 8\pi r\frac{M}{4\pi r^2 \rho}dn$$

$$dA = \frac{2M}{r\rho}dn \tag{11.19}$$

By putting the value of dA from equation (11.19) into equation (11.3), we get

$$dG = \gamma\frac{2M}{r\rho}dn \tag{11.20}$$

Comparing equation (11.16) and (11.20), we get

$$\gamma\frac{2M}{r\rho}dn = RT\ln\frac{P}{P_o}dn$$

$$\ln\frac{P}{P_o} = \frac{2\gamma M}{r\rho RT} \tag{11.21}$$

This mathematical expression (11.21) is known as Kelvin equation. According to this equation vapour pressure of liquid droplet is a function of density of liquid, radius of droplet, temperature, surface tension of liquid and molar mass of the liquid.

11.7 COLLOIDAL SYSTEM

Two phase system in which one is disperse phase and the other one is dispersion medium is called the colloidal system as shown in Fig. 11.1.

Dispersed phase is the phase which consists of colloidal particles. It is also called "inner phase" or "discontinuous phase". While, the phase in which the colloidal particles are dispersed is called dispersion medium. It is also called "outer phase" or "continuous phase". The layer which separates the inner and outer phase is called inter-phase or interface.

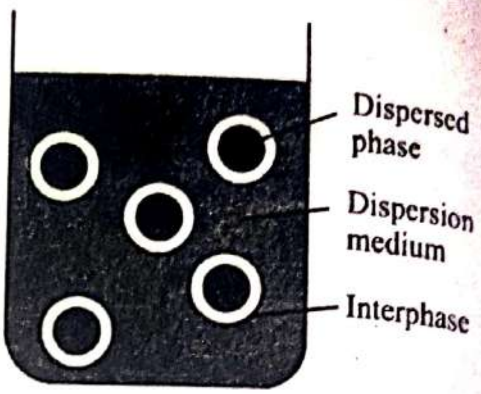


Fig. 11.2 Colloidal system showing disperse phase and dispersion medium

Widely used colloidal system may be one of three major types. It may be a sol, gel or emulsion as shown in Fig. 11.3.

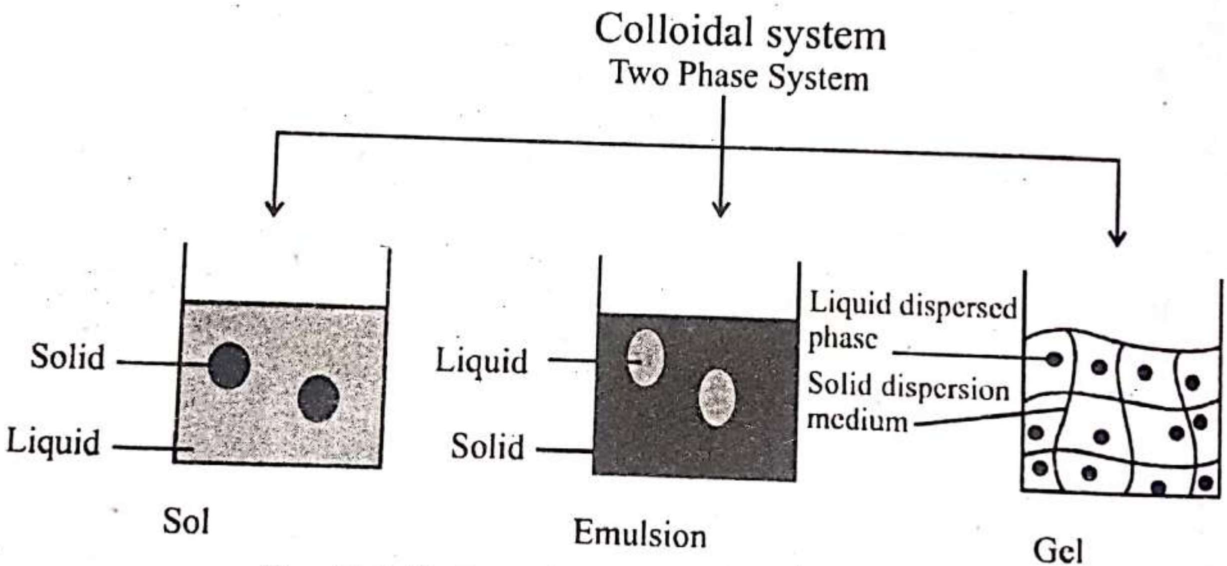


Fig. 11.3 Three major types of colloidal system

Sol

In sol, dispersed phase is solid and dispersion medium is liquid and size of sol particles lies between 1-1000 nm. If the range of particle size is 1-100 nm then the colloidal system is called nano system. Sols can be prepared by two methods as shown in Fig. 11.4. First one is the dispersion method which is also called top down approach or physical method or classical method. Using this technique, bulk material is broken into small particles. Many mechanical ways like cutting, milling, and grinding can be used for breaking. Second one is the aggregation method which is also called bottom up approach or chemical method. Chemical methods are excessively used to synthesize sol particles. Chemical methods like chemical reduction, thermal decomposition and photochemical reduction are presently in use for the synthesis of metal nanoparticles, because size, size distribution and shape of colloidal particles can be controlled by chemical methods.

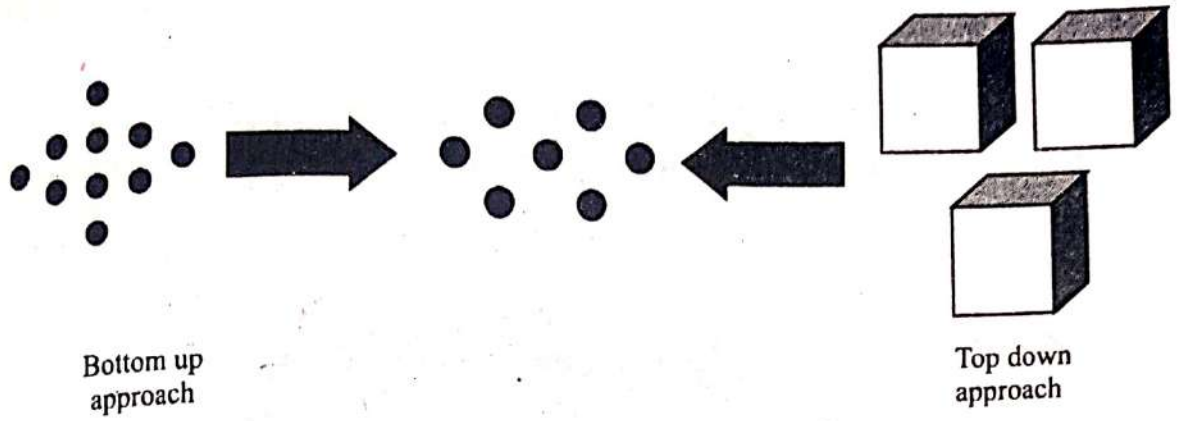


Fig. 11.4 Preparation of sol by top down and bottom up approach

In this chapter we will discuss gels and emulsions in detail.

11.8 EMULSION

The colloidal system which consists of two immiscible liquids is named as emulsion. In other words, an emulsion may be defined as "*the colloidal system in which liquid droplets are dispersed in another liquid.*" For example, milk is an emulsion in which fat droplets are dispersed in water. The basic component of emulsion is the emulsifying agent which maintains the stability of an emulsion.

Classification of Emulsion

Emulsions are classified into many kinds on different basis.

(1) On the Basis of Internal and External Phase

(a) Simple Emulsion

Simple emulsions are of two types as shown in Fig. 11.5. Oil in water (o/w) emulsion in which oil droplets are dispersed into water e.g.; milk. The other one is water in oil (w/o) emulsion in which water droplets are dispersed into oil such as greases.

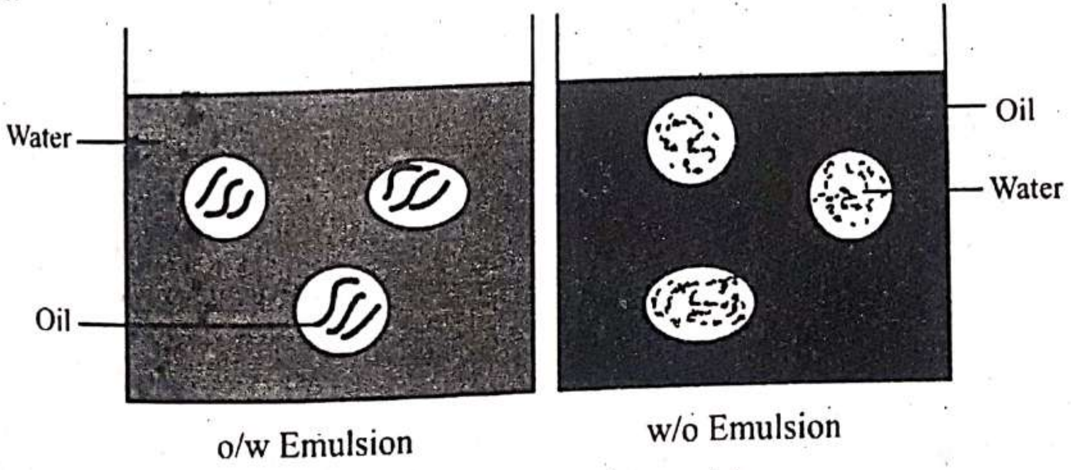


Fig. 11.5 Types of simple emulsions

(b) Double Emulsion

Double emulsions are also of two types. Water in oil in water (w/o/w) emulsion in which water droplets are dispersed in oil droplets of large size and then these oil droplets are further dispersed in water which acts as continuous phase as shown in Fig. 11.6 and vice versa for oil in water in oil (o/w/o) emulsion.

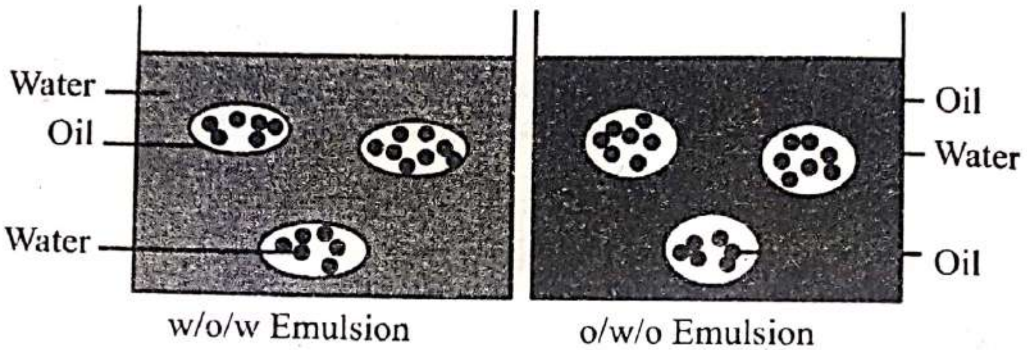


Fig. 11.6 Types of double emulsion; (a) w/o/w emulsion and (b) o/w/o emulsion

(c) Multiple Emulsion

There are two types of multiple emulsions. Emulsion in which water droplets are dispersed in oil, then oil droplets are further dispersed in the water and the whole system again is dispersed in oil is called w/o/w/o emulsion as depicted in Fig. 11.7. Similarly, when oil droplets are dispersed in water, then this system is dispersed in oil and the whole system is dispersed again in water is called o/w/o/w emulsion.

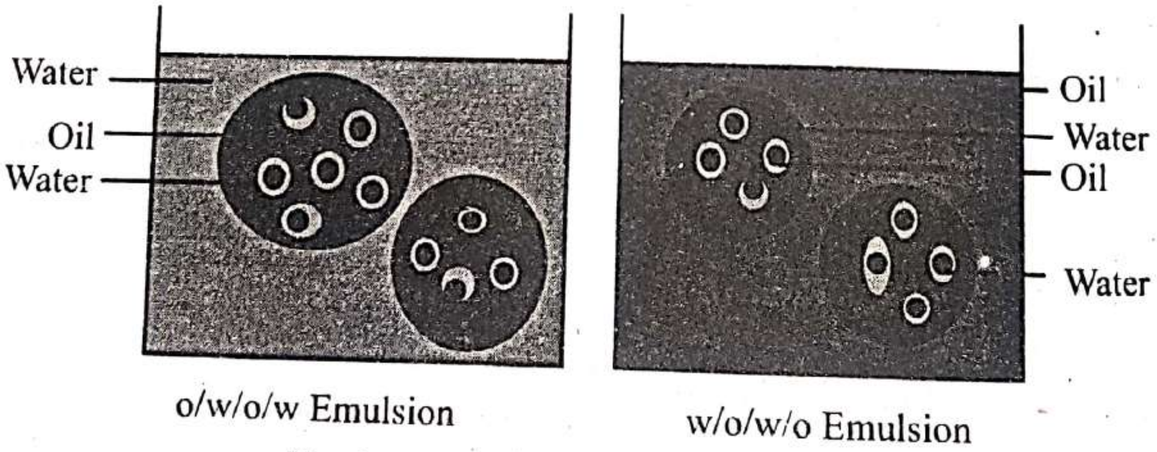


Fig. 11.7 Types of multiple emulsion

(2) On the Basis of Size of Droplet

(a) Macro Emulsion

Macro emulsion is the type in which particle size ranges from 1 to 50 μm. These emulsions are thermodynamically unstable but kinetically stable because of large particle size and diffusion of droplets become difficult. Macro emulsions can be stabilized by surfactants, polymers or small solid particles.

(b) Micro Emulsion

Micro emulsion consists of particles which are less than 1 µm. These emulsions are thermodynamically stable because the layer formation of emulsifier around the droplets of disperse phase is a spontaneous process.

(3) On the Basis of Emulsifier

(a) Pickering Emulsion

The emulsion in which solid particles act as an emulsifier is called Pickering emulsion.

(b) Non–Pickering Emulsion

While the emulsion in which emulsifier used is not in solid form is called non-pickering emulsion.

(c) Miceller Emulsion

In miceller emulsions, emulsifier is present in the form of micelles. In aqueous solution, when the concentration of emulsifier increases to a certain value, its molecules aggregate to form micelle. In the formation of micelle the hydrophobic (hydrocarbon) ends are directed towards the centre away from aqueous medium while its hydrophilic ends are in contact with water as shown in Fig. 11.8.

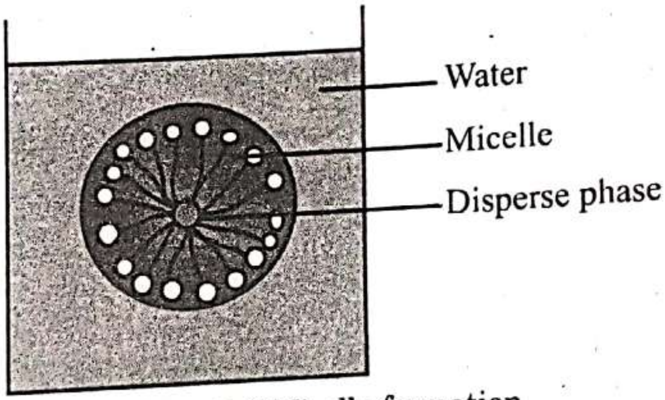


Fig. 11.8 Micelle formation

(4) On the Basis of Physical State of Dispersion Medium

(a) Liquid Emulsion

The emulsion in which dispersion medium and dispersed phase both are liquids is called liquid emulsion.

(b) Gel or Solid Emulsion

The emulsion in which dispersion medium is solid and dispersed phase is liquid, called solid emulsion. These are also known as gels.

(5) On the Basis of Outlook

(a) Watery Emulsion

When oil is dispersed in the water, we get watery emulsion.

(b) Oily or Greasy Emulsion

When water is dispersed in oil, we get oily or greasy emulsion.

(6) On the Basis of Appearance

(a) Transparent Emulsion

Micro emulsion is also named as transparent emulsion because its particle size is less than 1 μm. So, it will be transparent to visible light.

(b) Non–Transparent Emulsion

Macro emulsion is opaque or non-transparent emulsion because of its larger size particles.

11.9 CHARACTERIZATION OF SIMPLE EMULSION

Characterization of emulsions includes the determination of emulsion type as well as the determination of size of droplets.

11.9.1 Methods for Determination of Type of Emulsion

(1) Texture

The emulsion is observed, if it is oily or greasy in touch it means that the outer phase is oil and inner phase is water so, it is w/o emulsion and if emulsion is watery or creamy in touch then outer phase is water ad inner phase is oil so, it is o/w emulsion.

(2) Conductivity Method

The type of simple emulsion can be identified by conductivity method as shown in Fig. 11.9 (a). As we know that water is a good conductor of electricity than oil. The o/w emulsion can conduct electricity and w/o type emulsion cannot. Specific conductance of o/w emulsion is very high as compared to w/o emulsion.

(3) Mixing/Dilution Method

An emulsion can be diluted with the dispersion medium but not with dispersed phase. Consequently, if the emulsion is stable on addition of water into emulsion, it will be o/w emulsion. If phase separation occurs, with addition of water then this will be w/o emulsion as shown in Fig. 11.9 (b).

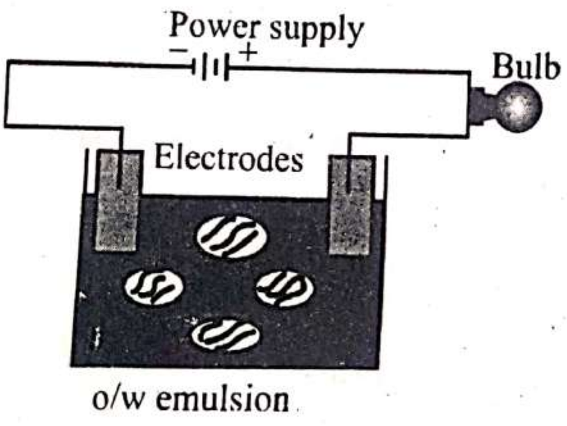


Fig. 11.9 (a) Conductivity circuit

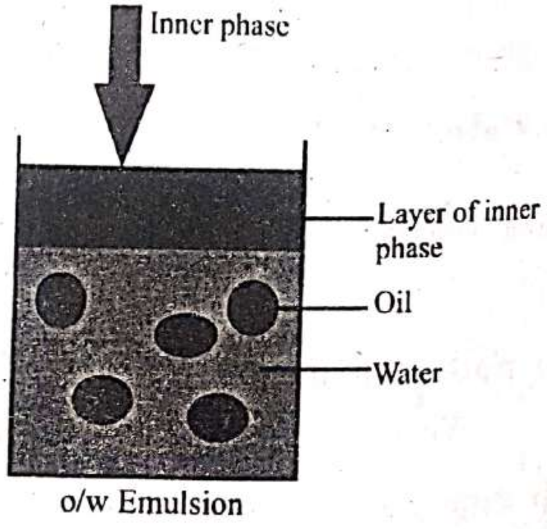


Fig. 11.9 (b) Mixing/dilution process

(4) Fluorescence Method

This method is based on the florescence property of some oils. *The material which has the property of absorbing shorter wavelength and emits longer wavelength is called fluorescent material.* As we know that some oils and organic liquids are fluorescent materials but water is not. When oil is the dispersion medium it will show fluorescence then this emulsion will be w/o emulsion, otherwise it is o/w emulsion.

(5) Dyeing

An emulsion can be characterized by selecting a specific dye that is soluble in one phase and insoluble in other phase e.g. methylene blue is a dye which is soluble in water and insoluble in oil. With the addition of methylene blue in an emulsion if emulsion color remains same as that of dye color, this is o/w emulsion. If color is not changed then this is w/o emulsion.

(6) Filter Paper Test

To check this test, dip the filter paper in 20% cobalt (II) chloride hexahydrate [$CoCl_2.6H_2O$] solution and dry it. Then dip this filter paper in emulsion and dry. If filter paper turns pink it will be o/w emulsion, and if its colour does not change then it is w/o emulsion.

(7) Magnetic Resonance Imaging (MRI)

Magnetic resonance imaging is used for the identification of dispersed phase and dispersion medium of emulsion. By taking a snap of emulsion with the help of MRI, we can distinguish that which one is the outer phase or inner phase.

(8) Phase Inversion Method

If we have an o/w emulsion, by addition of disperse phase (oil) initially flocculation occurs and two separate layers are formed. But if dispersed phase is added in large quantity a stage comes when emulsion will convert into w/o emulsion in which disperse phase is water and dispersion medium is oil. This is called phase inversion method as show in Fig. 11.10. On this basis, we can determine either emulsion is w/o or o/w.

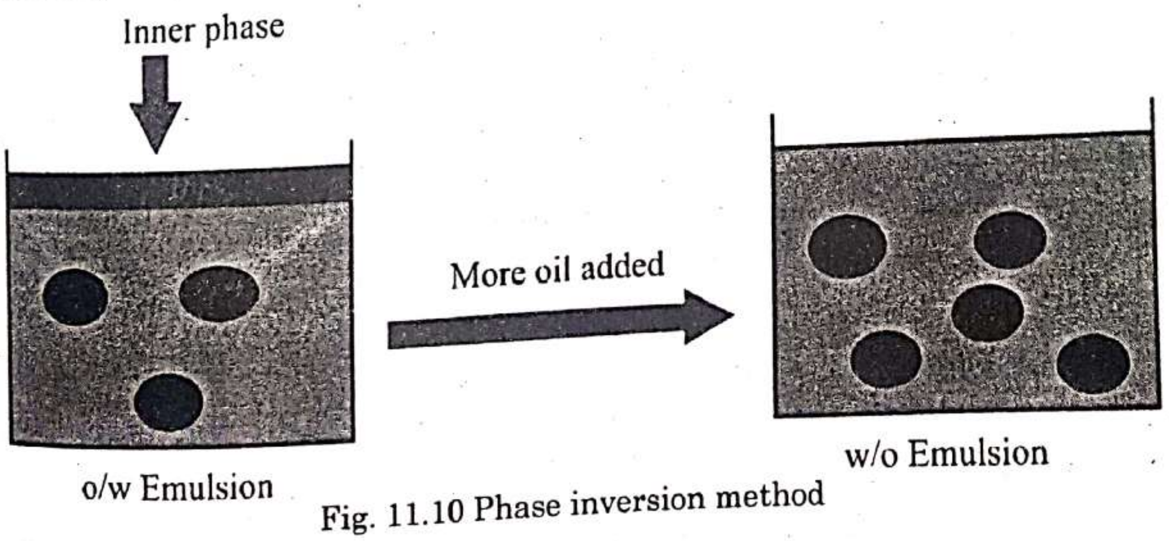


Fig. 11.10 Phase inversion method

11.9.2 Methods for the Determination of the Size of Droplet

Various methods are used to determine the size of droplet of dispersed phase of emulsion. Some are described here.

(1) Sedimentation under the Force of Gravity

The process of settling down of droplets of dispersed phase under force of gravity is called sedimentation. During sedimentation, two forces act on the particle, one of which is the force of gravity that acts vertically downwards ($F_g = mg$) and the other one is the drag force acting vertically upward ($F_D = 6\pi\eta rv$). As the particle moves downwards, its velocity increases due to increase in the gravitational force and as a result drag force also increases. After sometime equilibrium is established i.e. the two forces balance each other. At equilibrium, the velocity of particle will be maximum and remains constant and is called terminal velocity. Hence at equilibrium we may write as

$$F_g = F_D$$

$$mg = 6\pi\eta rv_t$$

By putting $m = \rho \times v$ in the above equation, we get

$$\rho vg = 6\pi\eta rv_t \tag{11.22}$$

Generally the density of medium is much less than that of the particles i.e. $\rho_m <<<< \rho$, this implies

$$\rho - \rho_m \approx \rho$$

Hence, equation (11.22) can become

$$(\rho - \rho_m)vg = 6\pi\eta rv_t \tag{11.23}$$

The volume of the spherical droplet is $\frac{4}{3}\pi r^3$, putting this value in the above equation, we get

$$(\rho - \rho_m)\frac{4}{3}\pi r^3 g = 6\pi\eta rv_t$$

$$v_t = \frac{2(\rho - \rho_m)r^2 g}{9\eta} \tag{11.24}$$

Equation (11.24) represents sedimentation velocity of the droplets. Replacing v_t by $\frac{dx}{dt}$ in this equation we get

$$\frac{dx}{dt} = \frac{2(\rho - \rho_m)r^2 g}{9\eta}$$

Let the particle be at a position x_1 at the time t_1 and at x_2 at a time t_2. Separating the variables in the above equation and integrating between these limits gives

$$\int_{x_1}^{x_2} dx = \frac{2(\rho-\rho_m)r^2g}{9\eta}\int_{t_1}^{t_2} dt$$

$$|x|_{x_1}^{x_2} = \frac{2(\rho-\rho_m)r^2g}{9\eta}|t|_{t_1}^{t_2}$$

$$(x_2-x_1) = \frac{2(\rho-\rho_m)r^2g}{9\eta}(t_2-t_1) \qquad (11.25)$$

Using equation (11.25), radius of the droplet can be calculated.

This process is very slow therefore, a modified method is developed called ultracentrifuge method or velocity sedimentation method.

(2) Ultracentrifugation Method

Sedimentation is a time consuming process as the droplets require a lot of time to settle down under the force of gravity. Settling process can take place at a faster rate using ultracentrifugation method, also known as velocity sedimentation method. In this method an external force is applied for the movement of droplet downward. As we know that centrifugal force is

$$F_c = \frac{mv^2}{x}$$

Where, x is the distance of the droplet from the axis of rotation, v is the velocity and m is the mass of the droplet.

Putting $v = xw$ in the above equation, we get

$$F_c = mxw^2$$

During the circular motion of the droplet, two forces act on it which include the centrifugal and the drag forces.

At the stage of equilibrium both the forces balance each other i.e.

$$F_d = F_c$$

$$6\pi\eta r v_t = mxw^2$$

Using equation (11.2), we can write

$$6\pi\eta r v_t = (\rho-\rho_m)xw^2V$$

By putting the value of V i.e. $\frac{4}{3}\pi r^3$, in the above equation, we get

$$6\pi\eta r v_t = (\rho - \rho_m) x w^2 \left(\frac{4}{3}\pi r^3\right)$$

$$v_t = \frac{2(\rho - \rho_m) x w^2 r^2}{9\eta}$$

As v_t is the rate of change of distance with respect to time, the above equation can also be written as

$$\frac{dx}{dt} = \frac{2(\rho - \rho_m) x w^2 r^2}{9\eta}$$

Let the particle be at position x_1 and x_2 at time t_1 and t_2 respectively. Separating the variables in the above equation and integrating between the limits of time and the corresponding distance, we get

$$\int_{x_1}^{x_2} \frac{dx}{x} = \frac{2(\rho - \rho_m) w^2 r^2}{9\eta} \int_{t_1}^{t_2} dt$$

$$\ln \frac{x_2}{x_1} = \frac{2(\rho - \rho_m) w^2 r^2}{9\eta} (t_2 - t_1) \qquad (11.26)$$

Where x_1 and x_2 can be easily measured using optical microscope during centrifugation. Hence the value of r can be calculated using equation (11.26) if all other parameters are known.

(3) Microscopic Methods

Transmission electron microscopy (TEM) and Scanning electron microscopy can also be used to determine the size of droplets of emulsion.

(4) Scattering Methods

Dynamic light scattering, small angle neutron scattering and small angle x-ray scattering are also used to determine the droplet size.

11.10 SURFACTANTS: EMULSIFIERS

"The substance which lowers the interfacial tension between two liquids and is used to stabilize the emulsion by increasing its kinetic stability is named as emulsifier". These can be classified as: surfactant, lyophillic colloid, finely divided solid particles and polymeric materials. Surfactants are surface active substances which can be used as emulsifier due to their amphiphilic structure.

Classification of Surfactants

Surfactants can be classified according to polar head groups into two main classes.

(1) Ionic surfactants

(2) Non-ionic surfactants

(1) Ionic Surfactants

The surfactants that have the ability to dissociate in water are called ionic surfactants e.g.;

$$CH_3(CH_2)_{11}SO_4^-Na^+ \rightleftharpoons CH_3(CH_2)_{11}SO_4^- + Na^+$$

Sodium dodecyl sulfonate

$$CH_3(CH_2)_{11}NH_3^+Cl^- \rightleftharpoons CH_3(CH_2)_{11}NH_3^+ + Cl^-$$

Lauryl amine hydrochloride

Ionic surfactant is further divided into three classes.

(a) Anionic Surfactants

Anionic surfactants contain anionic functional group at their head e.g. sodium dodecyl benzene sulfonate.

$$CH_3(CH_2)_{11}C_6H_4SO_3^-Na^+ \rightleftharpoons CH_3(CH_2)_{11}C_6H_4SO_3^- + Na^+$$

(b) Cationic Surfactants

Cationic surfactants are those in which hydrophillic portion contain cationic functional group e.g.; trimethyl dodecyl ammonium chloride.

$$C_{12}H_{25}N^+(CH_3)_3Cl^- \rightleftharpoons C_{12}H_{25}N^+(CH_3)_3 + Cl^-$$

(c) Zwitterionic or Amphoteric Surfactants

The surfactant which contains a head with positive and negative charges is called amphoteric/zwiterionic surfactant e.g. dodecyl betaine [$C_{12}H_{25}N^+(CH_3)_2CH_2COO^-$].

(2) Non-Ionic Surfactants

Non-ionic surfactants are those surfactants that have no charge group and can't be dissociated in water. Block copolymers of oxyethylene and oxybutylene are examples of non-ionic surfactants. Further non-ionic surfactants may be of two types either polymeric or non-polymeric surfactants.

11.11 PROPERTIES OF SURFACTANTS

Some important properties of the surfactants due to which they act as emulsifiers are discussed below

(1) Amphiphillic Structure

Surfactant molecule has amphiphillic structure, because it has a large hydrocarbons chain which is hydrophobic tail and hydrophilic head in nature as shown in Fig. 11.11.

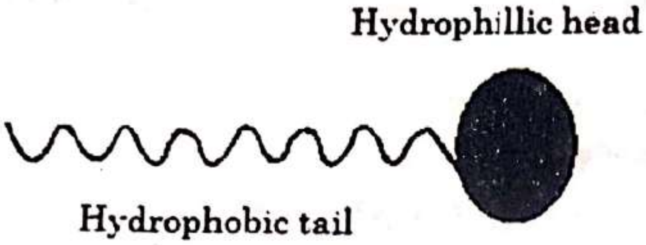


Fig. 11.11 Amphiphillic structure of surfactant.

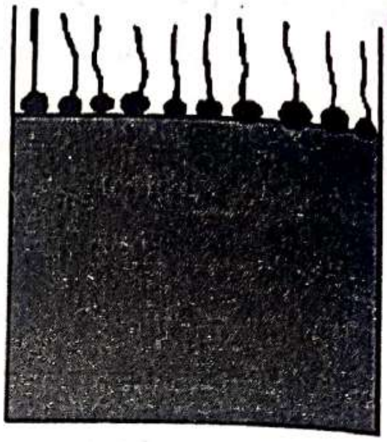


Fig. 11.12 Surfactant adsorption on air-water interfaces.

(2) Adsorption or Surface Activity

When surfactant is added into water it forms a layer at air-water interface by adsorption process as shown in Fig. 11.12. Surfactant adsorbs in such a way that its polar head is directed towards the aqueous phase and non-polar portion towards air phase and become adsorb on air-water interface.

(3) Reduction of Surface Tension

When surfactant adsorbs on the surface, then attraction on the surface atoms is balanced. Now downward force is balanced by upward force of surfactant. In this way, surfactant decreases the surface tension of liquid.

(4) Association or Micellization

"The process of micelle formation is called micellization". When a large quantity of surfactant is added in water after covering the whole air-water interface, the surfactant molecules will diffuse into the bulk material and they aggregate spontaneously to form a micelle as shown in Fig. 11.13.

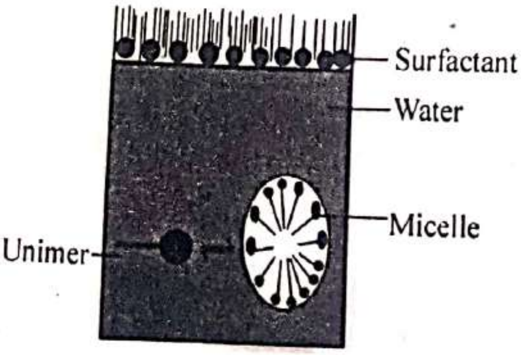


Fig. 11.13 Adsorption and micellization process

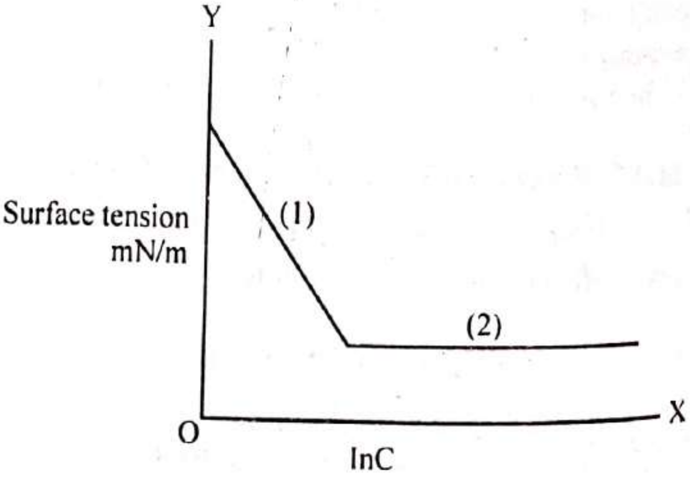


Fig. 11.14: Gibb's adsorption isotherm

11.12 GIBBS'S ADSORPTION EQUATION

"Relationship between the amount of surfactant adsorbed on interface and concentration of surfactant in solution at constant temperature is called Gibb's Adsorption isotherm"

Plot between surface tension and lnC as shown in Fig. 11.14 has two regions. In region (1), surface tension decreases with the increase in value of lnC. This region is called adsorption region or premiceller region and in region (2), surface tension remains constant with change of lnC, this region is called miceller region because micelle formation occurs in this region. Gibb investigated the change of surface tension of liquid with increase of surfactant concentration at constant temperature and formulated it in the form of an equation which is known as Gibb's adsorption isotherm. Mathematically it can be written as

$$\Gamma = \frac{-1}{RT}\left[\frac{d\gamma}{d\ln C}\right]_t \qquad (11.27)$$

Where, Γ is surface excess concentration and its units are mole/m^2 and it can be defined as *"no. of moles of surfactant adsorbed per unit area"*.

Where, $\left[\frac{d\gamma}{d\ln c}\right]_t$ is called the surface activity of surfactant at constant temperature.

Since, $\frac{d\ln C}{dC} = \frac{1}{C}$

So, $d\ln C = \frac{dC}{C}$

By putting value of $dlnC$ in equation (11.27), we get

$$\Gamma = \frac{-C}{RT}\left[\frac{d\gamma}{dC}\right]_t \qquad (11.28)$$

$$\Gamma = \frac{-C}{2.303RT}\left[\frac{d\gamma}{d\log C}\right]_t \qquad (11.29)$$

$\left[\frac{d\gamma}{d\ln C}\right]_t$ is the ability of surfactant molecules to reduce the interfacial tension between two liquids.

Significance of Gibb's Adsorption Equation

(1) This equation is used to study the adsorption on the surface of a liquid of a substance that dissolves in it.

When dγ/dC is positive, i.e. when the surface tension of the solution increases with concentration, Γ must be negative, and the body of solution is richer in solute than the surface, as in the case with many electrolytes and these substances are called surface inactive agents.

However when the surface tension of the solution decreases with concentration, i.e. $d\gamma/dC$ is negative, Γ is positive and the surface contains higher concentration of solute than the solution. The latter is the case with surface active agents. Positive surface activity is therefore is associated with the adsorption of solute from the solution by the surface of solution, while negative surface activity is due to the expulsion of solute from the surface.

The limiting value of the reduction in surface tension with concentration, i.e., $-\left(\frac{d\gamma}{dC}\right)_{C\to 0}$ is called surface activity of a substance.

(2) Gibb's equation can also be used to find out the adsorption of gas (vapours) on the surface of a liquid in which it is not soluble, by knowing the variation of γ with P of the adsorbate.

$$d\mu = RTd\ln P$$

$$\Gamma = -\frac{1}{RT}\frac{d\gamma}{d\ln P} = -\frac{P}{RT}\frac{d\gamma}{dP}$$

or

$$\Gamma = -\frac{1}{RT}\frac{\partial\gamma}{\partial\ln P} = -\frac{P}{RT}\frac{\partial\gamma}{\partial P}$$

(3) Area occupied by one molecule of adsorbate (a) can be found by using following equation

$$a = \frac{1}{N_A\Gamma}$$

Gibb's Adsorption Law

It was shown theoretically by Gibbs's that those substances which lower the surface tension of a solvent in which they are dissolve become concentrated in the surface layer, while the concentration of the substances which raise the surface tension is less in the surface layer than in the bulk of the solution.

$$-S = \frac{C}{RT}\frac{d\gamma}{dC}$$

$$S = -\frac{C}{RT}\frac{d\gamma}{dC}$$

Example 11.1

The slope of plot of surface tension vs. natural logarithm of surfactant was found to be -70N/m. Calculate the surface excess concentration at 25 °C in mol/m².

Solution

According to equation (11.27)

$$\Gamma = \frac{-1}{RT}\left[\frac{d\gamma}{d\ln C}\right]_T$$

Where, $\left[\frac{d\gamma}{d\ln C}\right]_T$ is the slope of the plot of surface tension vs. natural logarithm of the concentration of surfactant at a constant temperature T and is equal to -70Nm^{-1} at 298K as given in the question. Hence surface excess concentration will be

$$\Gamma = \frac{70Nm^{-1}}{\left(8.3143Jmol^{-1}K^{-1}\right)\left(298K\right)}$$

$$\Gamma = \frac{0.0283Nm^{-1}}{Nmmol^{-1}} = 0.0283molm^{-2}$$

11.13 CRITICAL MICELLE CONCENTRATION

Micelle formation occurs due to association of surfactant molecules into bulk phase. *"Single surfactant molecule is called unimer"*, and by the combination of unimers micelle formation occurs. *"The number of surfactant molecules present in a micelle is called aggregation number"*. If the micelle is in spherical form, then its radius is called hydrodynamic radius.

Micelles are formed at a certain concentration of surfactant and *"this minimum concentration at which process of micellization starts is called critical micelle concentration (CMC)"*. Below CMC micellization does not occur. Spherical micelle has two regions, hydrophilic region which is called corona and hydrophobic region which is called core as shown in Fig. 11.15. If the concentration of surfactant is less than the critical micelle concentration then it does not stabilize the emulsion.

The value of CMC of a surfactant depends upon temperature, hydrophilic-lipohilic balance (HLB) of surfactant and nature of solvent.

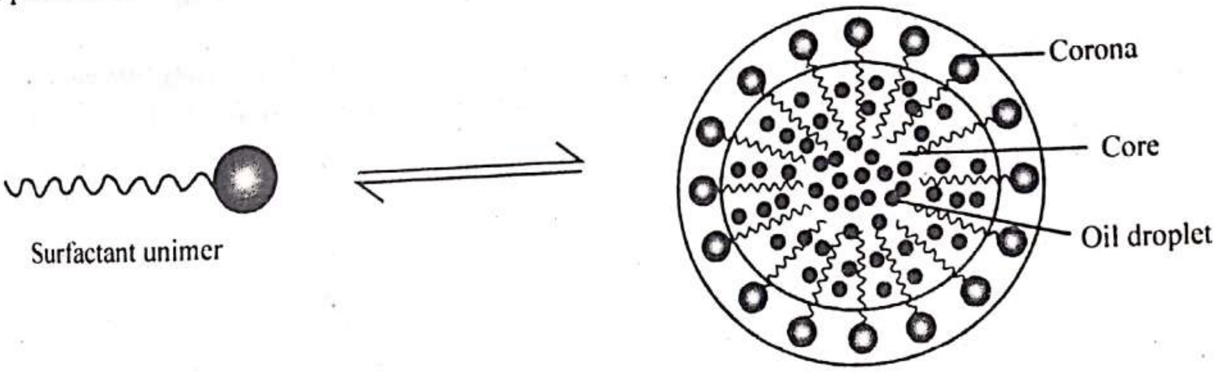


Fig. 11.15 Illustration of micellization and micelle structure

Determination of CMC of a Surfactant

Different methods for the determination of CMC are discussed below

(1) Surface Tension Measurement

Solutions of different concentration of surfactant are prepared and the surface tension of each solution is measured and a graph is plotted between surface tension versus natural logarithm of concentration of surfactant as shown in Fig.

11.16. At initial stages surface tension will decrease with the increase in lnC but after a certain concentration, value of surface tension will become constant. The concentration at which the surface tension of solution becomes constant is called CMC. Because at this concentration micelle formation starts. This method is applicable generally for the determination of CMC of nonionic surfactants.

(2) Conductivity Measurements

Solutions of different surfactant concentrations are prepared and the conductivity of solutions is measured. A graph is plotted between conductivity versus concentration as shown in Fig. 11.17. At initial stage, conductivity and concentration are linear to each other. At certain concentration, conductivity versus conc. plot gives a break. This break will give the value of CMC. Conductivity depends upon the mobility of unimers. After CMC unimers combine and form micelle. Because the mobility of micelle is less than that of unimer so, slope of plot changes at CMC.

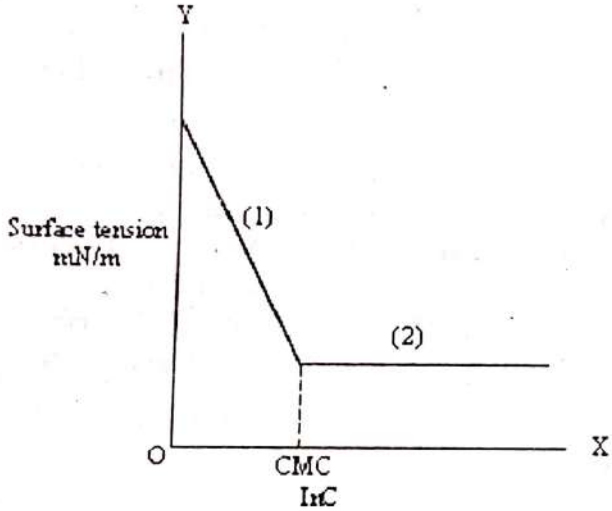


Fig. 11.16 Plot of surface tension versus lnC

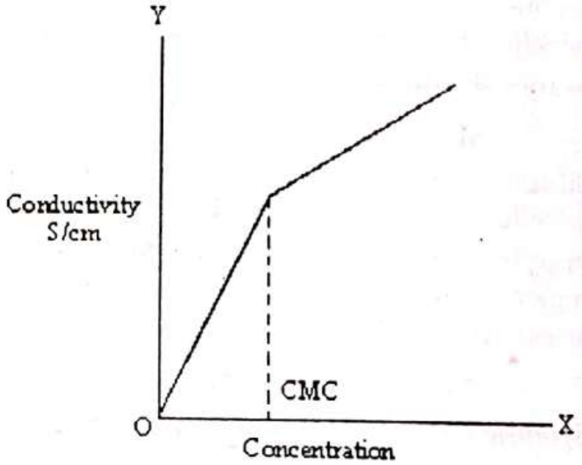


Fig. 11.17 Plot of conductivity versus concentration of surfactant

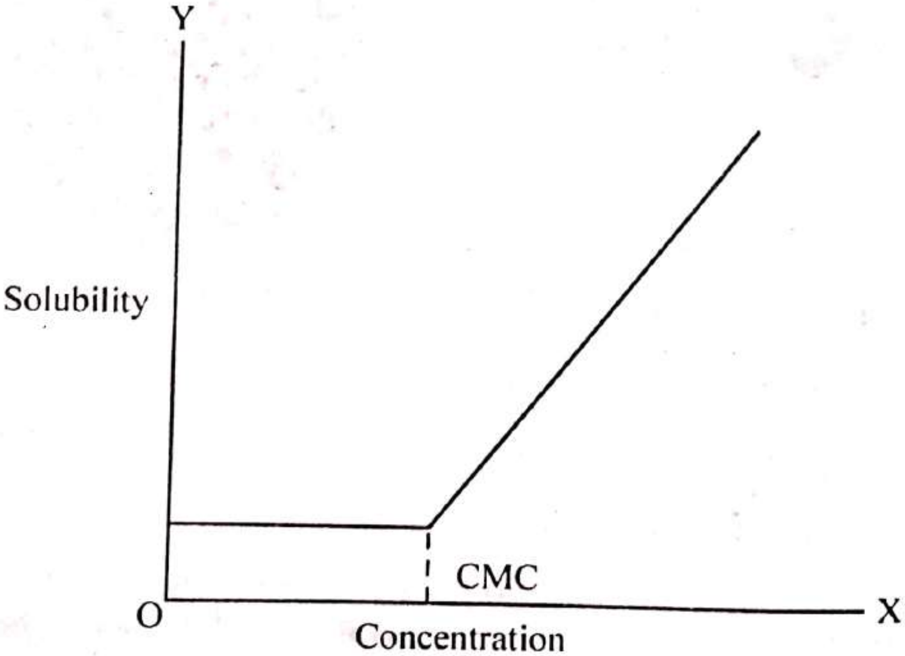


Fig. 11.18 Plot of solubility versus concentration of surfactant

(3) Solubility Measurements

A substance is taken that is insoluble in water. Solutions of different concentrations of surfactant are prepared and the substance that is insoluble in water is added. At lower concentration of surfactant the substance is not soluble because surfactant is present at interface only. But when concentration of surfactant approaches the CMC and surfactant molecules goes in to the bulk then they can solubilize the substance. As a result of which solubility of the substance increases rapidly. Break point of plot of solubility of the substance as function of concentration of surfactant gives the value of CMC of surfactant as shown in Fig. 11.18.

11.14 MICELLIZATION OF NON-IONIC SURFACTANT

Micellization is a reversible process. Initially the rate of formation of micelle is greater than the rate of formation of unimer. A stage at which rate of both processes becomes equal is called dynamic equilibrium. The value of the concentration of the surfactant at the stage of dynamic equilibrium between unimer and micelle is called CMC. Dynamic equilibrium between unimer and micelle of surfactant A can be shown as

$$NA \rightleftarrows A_N$$

Dividing by N, we get

$$A \rightleftarrows \frac{1}{N} A_N$$

The equilibrium constant can be written as

$$K = \frac{[A_N]^{1/N}}{[A]}$$

When N is very large then 1/N = 0 and [A]→CMC then,

$$K = \frac{[A_N]^0}{[A]}$$

$$K = \frac{1}{[CMC]} \tag{11.30}$$

According to thermodynamics, Gibb's free energy for micellization is given by

$$\Delta F_{mic} = -RT \ln K \tag{11.31}$$

By putting value of K from equation (11.30) into (11.31), we get

$$\Delta F_{mic} = -RT \ln \frac{1}{CMC}$$

$$\Delta F_{mic} = RT \ln CMC$$

This is the relation between free energy of micellization and CMC. Its value may be positive or negative if value is negative then the process will be spontaneous and if the value is positive then the process will be non-spontaneous.

Value of ΔF_{mic} is negative for non-ionic surfactants and the process of micellization is spontaneous. From equation (11.31) we can find relation between lnCMC and temperature.

$$\ln CMC = \frac{\Delta F_{mic}}{RT}$$

Above equation shows that with the increase in temperature for a particular liquid CMC decreases. Hence CMC is temperature dependant.

11.15 THERMODYNAMICS OF MICELLIZATION

(1) Free Energy of Micellization

ΔF_{mic} is called free energy of micellization and it can be determined from the value of CMC using following relation

$$\Delta F_{mic} = RT \ln CMC$$

Its units are kJ/mole. If the value of ΔF_{mic} is negative then the process is spontaneous. lnCMC is a unit less or dimensionless quantity so it is written in terms of mole fraction.

$$\Delta F_{mic} = RT \ln X_{CMC} \qquad (11.32)$$

X is the mole fraction of solute or surfactant. If X_{CMC} is less than 1 then ΔF_{mic} will be negative and process is spontaneous.

(2) Enthalpy of Micellization

"Heat absorbed or evolved during micellization when one mole of micelle is formed is called enthalpy of micellization". It is represented as ΔH_{mic} and its units are kJ/mole. If ΔH_{mic} is negative then the micellization process is exothermic and if the ΔH_{mic} is positive then the process is endothermic. But in case of non-ionic surfactant it is always positive.

$$\Delta F_{mic} = RT \ln X_{CMC}$$

By differentiating above equation with respect to T

$$\frac{\partial(\Delta F_{mic})}{\partial T} = R\left[T\frac{\partial \ln X_{CMC}}{\partial T} + \ln X_{CMC}\right]$$

$$\frac{\partial(\Delta F_{mic})}{\partial T} = RT\frac{\partial \ln X_{CMC}}{\partial T} + R\ln X_{CMC}$$

By multiplying above equation with T

$$T\frac{\partial \Delta F_{mic}}{\partial T} = RT^2\frac{\partial \ln X_{CMC}}{\partial T} + RT\ln X_{CMC}$$

$$T\frac{\partial \Delta F_{mic}}{\partial T} = RT^2\frac{\partial \ln X_{CMC}}{\partial T} + \Delta F_{mic}$$

$$\Delta F_{mic} - T\frac{\partial \Delta F_{mic}}{\partial T} = -RT^2 \frac{\partial \ln X_{CMC}}{\partial T} \tag{11.33}$$

According to Helmholtz equation

$$\Delta F_{mic} - T\frac{\partial \Delta F}{\partial T} = \Delta H_{mic} \tag{11.34}$$

By comparing equation (11.33) and (11.34), we get

$$\Delta H_{mic} = -RT^2 \frac{\partial \ln X_{CMC}}{\partial T}$$

$$\frac{\Delta H_{mic}}{RT^2}\partial T = \partial \ln X_{CMC}$$

By integrating above equation, we get

$$-\frac{\Delta H_{mic}}{R}\int \frac{1}{T^2}\partial T = \int \partial \ln X_{CMC}$$

$$\ln X_{CMC} = \frac{\Delta H_{mic}}{R}\left(\frac{1}{T}\right) + c \tag{11.35}$$

This is an equation of straight line with intercept form as shown in Fig. 11.19.

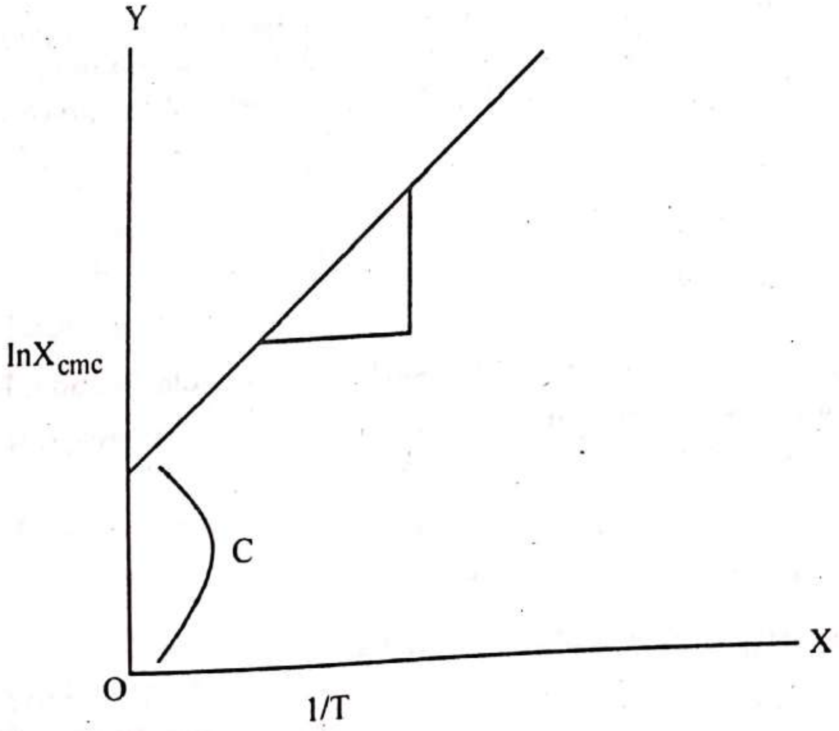


Fig. 11.19 Plot of lnXCMC versus 1/T

ΔH_{mic} can be determined from the slope as

$$\text{slope} = \frac{\Delta H_{mic}}{R}$$

$$\Delta H_{mic} = \text{slope} \times R$$

Slope is positive which shows that ΔH_{mic} is positive which indicates that process is endothermic.

(3) Entropy of Micellization

It is represented by ΔS_{mic} and its units are $JK^{-1}mole^{-1}$. Entropy of micellization is zero or positive for spontaneous process (according to 2nd law of Thermodynamics). When surfactant diffuse into the bulk, then it breaks the structure of water and creates disorderness among the water molecules, hence entropy is increased. When micelle is formed, then due to hydrophobic core water is expelled to the surrounding due to hydrophobic core, hence entropy increased. Both these factors are the causes behind increase in entropy of the system. Entropy of micellization can be calculated using fundamental relation of thermodynamics as

$$\Delta F_{mic} = \Delta H_{mic} - T\Delta S_{mic}$$

$$\Delta S_{mic} = \frac{\Delta H_{mic} - \Delta F_{mic}}{T} \qquad (11.36)$$

Example 11.2

The value of CMC of surfactant poly(oxyethylene)-poly(oxybutylene)-poly(oxyethylene) $[E_{20}B_{10}E_{20}]$ was determined and it was found to be 0.56g/L at 25°C. Calculate the value of ΔG_{mic} and comment on spontaneity of the process.

Solution

As we know that

$$\Delta F_{mic} = RT \ln X_{CMC}$$

Where, X_{CMC} is the CMC of the surfactant in mole fraction. If n_1 and n_2 are the number of moles of surfactant and that of water (solvent) respectively, then mole fraction of the surfactant can be calculated as

$$X_{CMC} = \frac{n_1}{n_1 + n_2} = \frac{0.00028}{0.00028 + 55.56} = 5.04 \times 10^{-6}$$

Hence ΔF_{mic} can be easily calculated as

$$\Delta F_{mic} = (8.3143)(298)\ln\left(5.04 \times 10^{-6}\right) = -3.02 \times 10^{4}\,\text{Jmol}^{-1}$$

11.16 TECHNIQUES USED TO STUDY MICELLIZATION PARAMETERS

(1) Surface Tensiometry

Surface tension measurement can be used for the determination of CMC, critical surface tension γ_{cmc} (surface tension at CMC), surface pressure, free energy of micellization, enthalpy of micellization and entropy of micellization. Fig. 11.20 gives plot of surface tension as a function of natural logarithem of concentration of surfactant. The value of CMC can be determined from the plot. The value of critical surface tension corresponds to CMC can be measured from the plot in Fig. 11.20. The difference between surface tension of pure water and surfactant containing water at various concentration gives value of surface pressure ($\pi = \gamma_0 - \gamma_{cmc}$). Free energy of micellization, enthalpy of micellization and entropy of micellization can be determined using equations (11.11), (11.14) and (11.15) respectively.

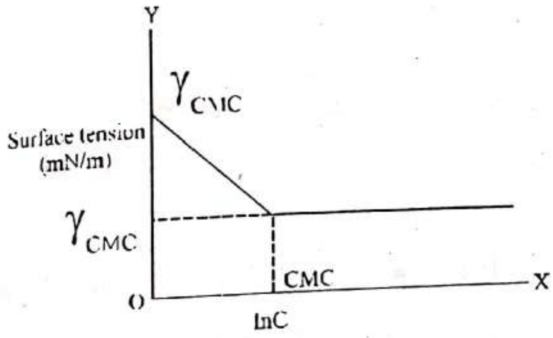


Fig. 11.20 Plot of surface tension versus lnC

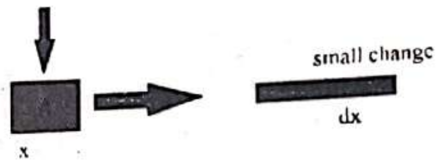


Fig. 11.21 Deformation of material

(2) Viscosity and Density Measurements

The viscosity and density measurements give information about elasticity of micelles and water contents in core and corona region of micelles. The term viscosity is associated with rheology which is a science of flow and deformation of materials.

The deformation of material is the change in shape under external force as shown in Fig. 11.21.

The force applied per unit area is called shear stress and its unit are Nm^{-2}. Mathematically shear stress can be written as

$$\tau = \frac{F}{A}$$

The change in length is measured in term of shear strain which is

$$\gamma = \frac{\Delta X}{X}$$

According to Hook's Law of deformation of materials, shear stress and shear strain are directly related to each other i.e.

$$\tau \propto \gamma$$

$$\tau = G\gamma$$

Where proportionality constant G is called Young's modulus. The rate of change of strain with respect to time is called shear rate and its unit are s^{-1} and mathematically can be written as

$$\text{Shear rate} = \gamma^{o} = \frac{d\gamma}{dt}$$

Newton gave a relation between shear stress and shear rate to define the viscosity and this relation is called Newton law of viscosity which is given below

$$\tau \propto \gamma^{o}$$

$$\tau \propto \frac{d\gamma}{dt}$$

$$\tau = \eta \frac{d\gamma}{dt}$$

Where η is viscosity of material on which deformation occurs

$$\eta = \tau \frac{dt}{d\gamma}$$

Unit of η are Nsm^{-2} while in System International (S.I) its unit are $Kgm^{-1}s^{-1}$.

τ represents absolute or dynamic viscosity. If material has the ability to follow the Newton law of viscosity is called the Newtonian material otherwise Non-Newtonian material.

Relative viscosity (η_{rel}) and specific viscosity (η_{sp}) are unitless quantities and represented by following equations.

$$\eta_{rel} = \frac{\eta_{\text{solution}}}{\eta_{\text{solvent}}}$$

$$\eta_{sp} = \eta_{rel} - 1$$

Reduced viscosity (η_{red}) is the ratio of specific viscosity to the concentration of surfactant and is represented by

$$\eta_{red} = \frac{\eta_{sp}}{c}$$

By plotting a graph between concentration and reduced viscosity as shown in Fig. 11.22. The intrinsic viscosity [η] can be determined and defined as *"the value of reduced viscosity when concentration approaches to zero"*.

[η] can be used to estimate the quantity of water inside the micelle. We can derive an expression for water contents inside the micelle and intrinsic viscosity. Water contents are decreased by increasing the temperature of the system, size of micelle also decreases as shown in Fig. 11.22.

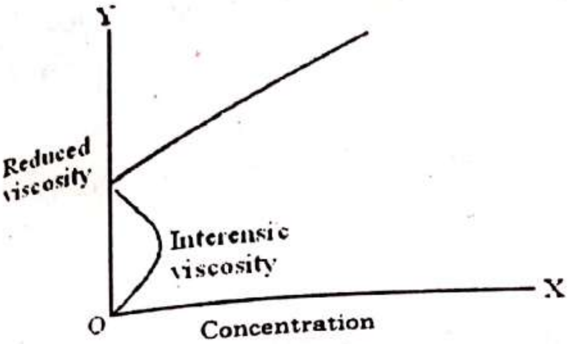


Fig. 11.22 Plot of reduced viscosity versus concentration

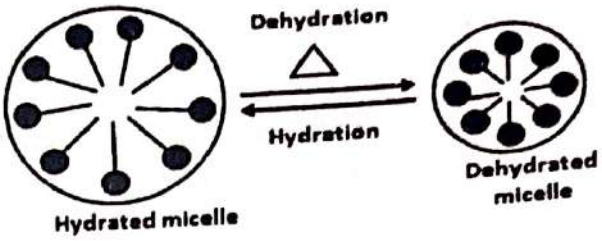


Fig. 11.23 Decrease in size of micelle due to expulsion of water

Volume of hydrated micelle = V_h

Volume of anhydrous micelle = V_a

Volume of water in micelle $= (V_h - V_a)$

Mass of water in micelle $= \rho_o (V_h - V_a)$

Mass of water in one mole of micelle $= \rho_o N_A (V_h - V_a)$

1 g of water in 1 g of micelle is called hydration value. So,

$$\text{Hydration value} = \frac{\rho_o N_A (V_h - V_a)}{\text{Molar mass of micelle}}$$

$$\text{Hydration value} = \frac{\rho_o N_A (V_h - V_a)}{M_{mic}}$$

$$W_h = \frac{\rho_o N_A V_a}{M_{mic}} \left(\frac{V_h}{V_a} - 1 \right) \tag{11.37}$$

Where, υ' is called partial specific volume and is determined by following relation

$$\upsilon' = \frac{N_A V_a}{M_{mic}}$$

By replacing $N_A V_a / M_{mic}$ with υ' in equation (11.37), we get

$$W_h = \upsilon' \rho_o \left(\frac{V_h}{V_a} - 1 \right) \tag{11.38}$$

Einstein gave a relation among intrinsic viscosity, partial specific volume and, volume of hydrated and anhydrated micelle by considering micelles as sphere suspended in liquid i.e.

$$\frac{[\eta]}{2.5\upsilon'} = \frac{V_h}{V_a} \tag{11.39}$$

By putting value of V_h/V_a from equation (11.39) into (11.38), we get

$$W_h = \upsilon\rho_o\left(\frac{[\eta]}{2.5\upsilon'}-1\right)$$

By using above equation hydration value can be calculated. The value of υ' can be determined using following equation

$$\rho = (1-\upsilon'\rho_o)C+\rho_o$$

This is an equation of straight line in intercept form whose intercept is ρ_o and slope is $1-\upsilon'\rho_o$. And $\frac{[\eta]}{\upsilon'}$ is the shape factor of micelle which is equal to υ.

If micelle is rigid, anhydrous and spherical then $\nu = \frac{[\eta]}{\nu'} = 2.5$

Hence, viscosity and density measurements give information about elasticity of micelles, water contents in a micelle and shape of micelles.

(1) Dynamic Light Scattering (DLS)

Dynamic light scattering is used to determine the size of micelles, size distribution of micelles and variation in size of micelles with change in temperature.

Light scattering is of two types.

(a) Rayleigh Scattering

When size of a particle is smaller than wavelength of radiation, then Rayleigh scattering occurs. Wavelength of incident and scattered radiation remains same in it. This is elastic scattering. If particle size is larger, then scattered radiations reach the detector with phase difference and result in interference effect.

(b) Raman Scattering

It is inelastic scattering and is exhibited by relatively larger particles. Here, wavelength of scattered radiation is not equal to that of incident one, so if energy is absorbed by molecule then scattered photons will be of lower frequency and if photons gain energy from molecule then scattered radiation will be of higher frequency. Fig. 11.24 depicts the scattering of light in miceller solution.

The magnitude of scattering vector (q) can be written as

$$q = \frac{4\pi n}{\lambda}\left(\sin\frac{\theta}{2}\right)$$

Where α is the wavelength of light, θ is scattering angle and n is refractive index of solvent. Fig. 11.25 shows plot of intensity of scattering light as a function of time.

$$\Gamma = \frac{1}{\tau}$$

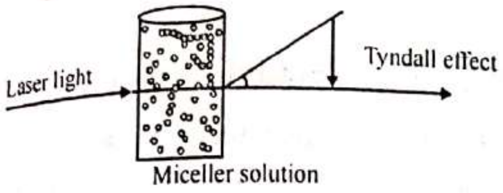


Fig. 11.24 Scattering of light

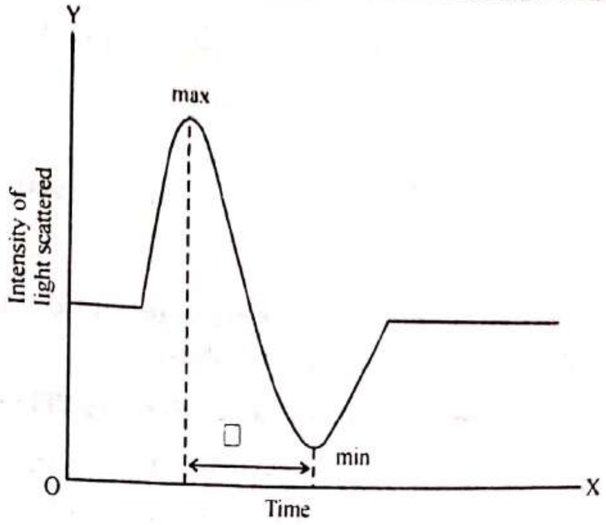


Fig. 11.25 Intensity of scattered light as a function of time

Γ is the decay rate and τ is the delayed period which is the difference between the maximum and minimum value of scattering intensities. Maximum scattering occurs when particle is in the path of light and scattering decreases when particles move away from light path. Decay rate is related to scattering vector as

$$\Gamma = Dq^2$$

Where D is the diffusion co-efficient and q is scattering vector.

According to Stokes-Einstein equation diffusion coefficient is given by

$$D = \frac{k_B T}{6\eta\pi R_h} \tag{11.40}$$

Where, k_B is Boltzmann constant, R_h is the hydrodynamic radius of micelle, T is absolute temperature and η is the viscosity of solvent. Equation (11.40) gives the value of hydrodynamic radius.

11.17 THEORIES OF EMULSION TYPE

Theories of emulsion type fall into two categories

(1) Qualitative Theories

(2) Quantitative Theories

11.17.1 Qualitative Theories

(1) Theory of Interfacial Tension

According to this theory, the interfacial tension between oil and surfactant and that between water and surfactant determines the type of emulsion. If the surface tension between water and surfactant is greater than that between oil and surfactant i.e.; $\gamma_{ws} > \gamma_{os}$, then water in oil emulsion is formed and vice versa.

(2) Banscroft's Rule of Emulsion Type

According to Bancroft's rule

The liquid in which emulsifier is more soluble acts as a continuous phase and the other liquid acts as discontinuous phase

or

The liquid having more ability to wet the emulsifier acts as continuous phase and other acts as dispersed phase.

(3) Emulsification and Wetting (Theory Based on Contact Angle)

The displacement of a fluid from a surface by another fluid is termed as wetting. Commonly term wetting is used for displacement of air from the surface of a solid by a liquid. Three immiscible phases are involved in wetting process. Out of these three phases, at least two phases are fluids. Wetting ability of a fluid is measured in terms of contact angle as shown in Fig. 11.26. When the contact angle of droplet of liquid with the solid surface is low, its wetting ability is high whereas a large contact angle corresponds to low wetting ability.

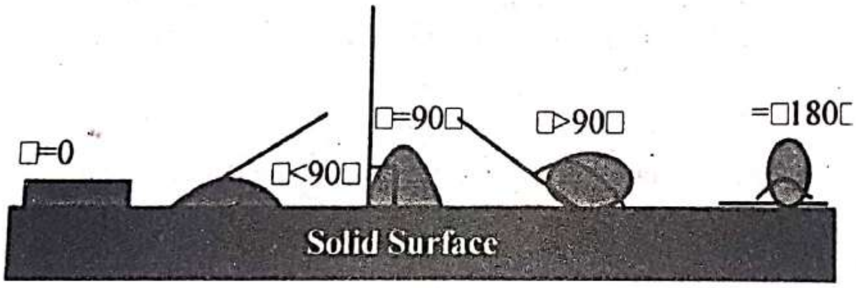


Fig. 11.26 Contact angle and wetting

Measurement of Contact Angle

When a drop is static, then the sum of all the forces along x-axis becomes zero.

According to Young's equation,

$$\gamma_{vs} = \gamma_{sl} + \gamma_{lv}\cos\theta \tag{11.41}$$

Where, $\gamma_{vs}, \gamma_{sl}, \gamma_{lv},$ is the interfacial tension between vapor and solid, solid and liquid and liquid and vapor respectively. While, θ is the contact angle between solid and liquid as shown in Fig. 11.27.

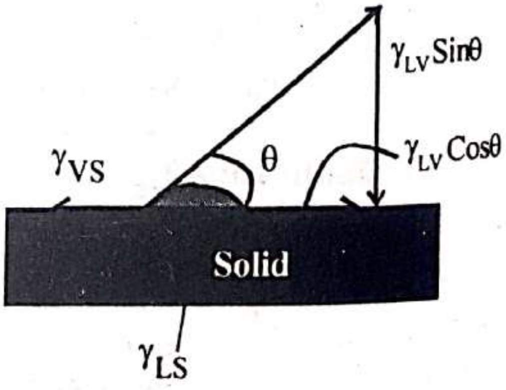


Fig. 11.27 Measurement of contact angle

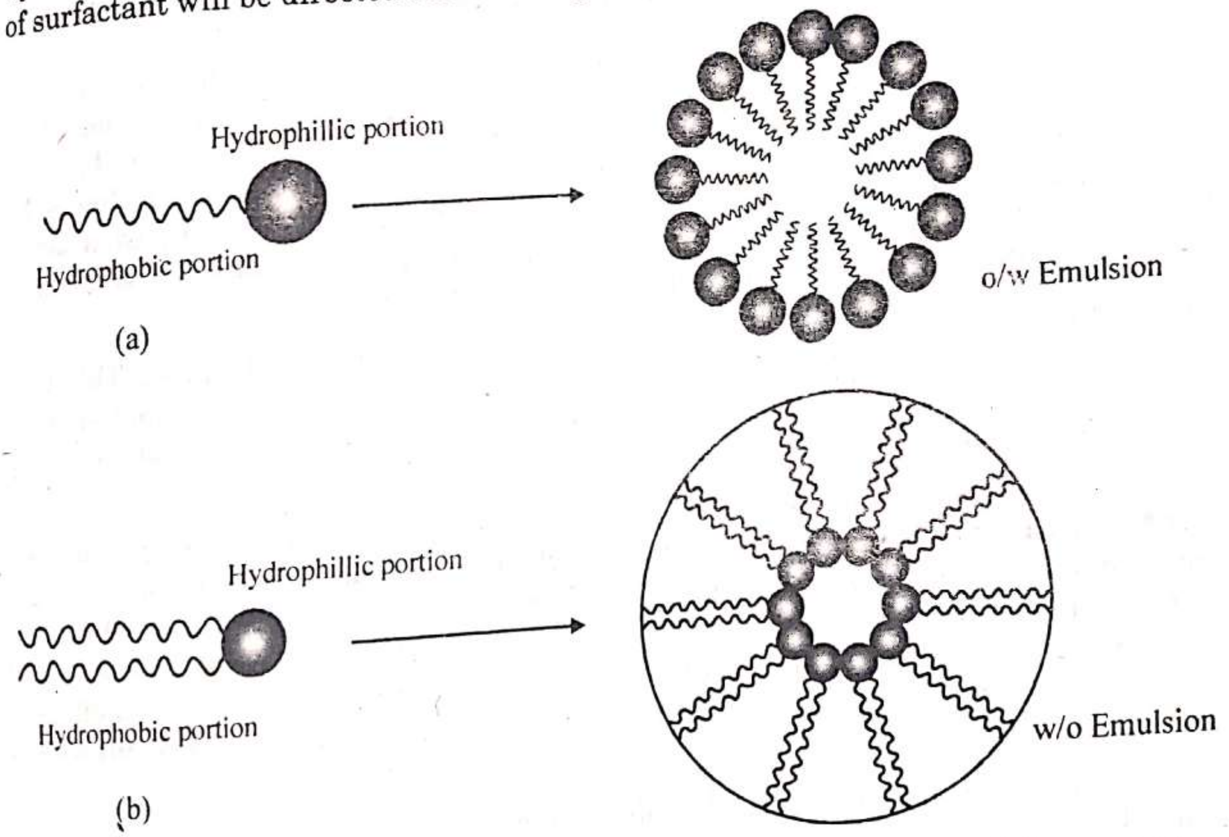
If the values of the interfacial tensions are known then we can determine the value of contact angle. From equation (11.41), we get

$$\cos\theta = \frac{\gamma_{vs} - \gamma_{sl}}{\gamma_{lv}} \tag{11.42}$$

According to equation (11.42) when we add surfactant into a liquid, it decreases its surface tension (γ_{lv}) and increases value of cosθ but decreases value of contact angle. In other words, surfactant increases the wetting ability of a liquid by lowering its surface tension. Such chemical substances are called wetting agents. The liquid having high wetting ability will serve as continuous phase in emulsion. If the angle of contact of the droplet with emulsifier is less than 90° then the liquid will act as a dispersed phase and vice versa.

Orientation Wedge Theory

In orientation theory, the type of emulsion depends upon the cross sectional area of hydrophillic and hydrophobic end of the surfactant. If the cross sectional area of hydrophilic end of surfactant is larger than hydrophobic end then surfactant adopts configuration in a micelle in such a way that hydrophobic portion will remain outward to form o/w emulsion as shown in Fig. 11.28 (a). If cross sectional area of hydrophobic group is greater than that of hydrophilic portion then hydrophobic side of surfactant will be directed outward to give w/o emulsion as shown in Fig. 11.28 (b).



(a)

(b)

Fig. 11.28 (a) Orientation of surfactant having hydrophillic end with large cross section, (b) orientation of surfactant having hydrophobic end with large cross section

For example the ability of the formation of w/o emulsion increases from sodium salt to aluminum salt in the following surfactants (sodium oleate, calcium oleate and aluminium oleate respectively) due to inverse in cross sectional area of hydrophobic part of surfactant.

$H_3C\left(CH_2\right)_{16}COONa$

Sodium oleate

$\left(H_3C-\left(CH_2\right)_{16}COO^-\right)_2Ca^{2+}$

Calcium oleate

$\left(H_3C-\left(CH_2\right)_{16}COO^-\right)_3Al^{3+}$

Aluminium oleate

Example 11.3

Arrange the following surfactants according to increasing order of ability to form o/w emulsion. $E_{20}B_{10}E_{20}$, $E_{30}B_{10}E_{30}$, $E_{48}B_{10}E_{48}$. Where, E is oxyethylene unit and B is oxybutylene unit of block copolymer.

Solution

The ability of the given surfactants to form o/w emulsion will be $E_{48}B_{10}E_{48} > E_{30}B_{10}E_{30} > E_{20}B_{10}E_{20}$. This is due to the fact that solubility of surfactant in water increases with increase of block length of hydrophilic unit e.g.; E.

11.17.2 Quantitative Theory

Kinetic Theory of Emulsion Type

This theory was proposed by Davis and Rideal in 1963.

Postulates of kinetic theory of emulsion type are

(i) According to this theory, the type of emulsion depends upon the relative rates of coalescence of droplets of opposite phases. If the rate of aggregation of oil droplets is greater than that of water then, oil droplets fuse together and form continuous phase, as a result water in oil emulsion is formed. Similarly, if rate of coalescence of oil droplets is less than that of water, then oil in water emulsion is formed, where as in case of equal rates of coalescence, unstable emulsion is formed and phase separation occurs.

(ii) Emulsifier forms a film around the droplets of dispersed phase. This film prevents the droplet to aggregate and hence, acts as a barrier which may be electrical, in case of ionic surfactant or mechanical in case of non-ionic surfactant.

The rate of coalescence or aggregation of emulsion depends on particle size, number of particles of dispersed phase and diffusion coefficient. It increases with the increase in particle size due to the greater probability of aggregation. With the increase in the number of droplets of dispersed phase, due to the greater number of collision rate of aggregation increases. Similarly, higher diffusion coefficient corresponds to higher speeds and greater probability of collisions, as a result rate of coalescence increases.

Davis and Rideal derived the following mathematical relation to describe the dependence of the rate of coalescence on above mentioned factors.

$$-\frac{dn}{dt} = 4\pi Drn^2 \tag{11.43}$$

Where, D is the diffusion co-efficient, r is the collision diameter of droplet and n is the number of particle of disperse phase.

Equation (11.43) is applicable only if all collisions are effective but in actual it is not possible, therefore a factor $e^{-E/kT}$ is introduced. Hence, equation (11.43) will be

$$-\frac{dn}{dt} = 4\pi Drn^2 e^{-\frac{E}{kT}} \tag{11.44}$$

Separating the variables and integrating equation (11.44), we get

$$-\int\frac{dn}{n^2} = 4\pi Dre^{-\frac{E}{kT}}\int dt$$

$$\frac{1}{n} = 4\pi Dre^{-\frac{E}{kT}}t + c \tag{11.45}$$

This is an equation of straight line in intercept form with slope $4\pi Dre^{-\frac{E}{kT}}$.

According to Stoke- Einstein equation we know

$$D = \frac{kT}{6\pi\eta a} \tag{11.46}$$

Where, a is the radius of single droplet and

$$r = 2a \tag{11.47}$$

Putting the value of D and r from equation (11.46) and (11.47) respectively into equation (11.45), we get

$$\frac{1}{n} = 4\pi\frac{kT}{6\pi\eta a}2ae^{-\frac{E}{kT}}t + c$$

$$\frac{1}{n} = \frac{4}{3}\frac{kT}{\eta}e^{-\frac{E}{kT}}t + c \tag{11.48}$$

This is an equation of straight line in intercept form, the slope of which is equal to $\frac{4}{3}\frac{kT}{\eta}e^{-\frac{E}{kT}}$. Hence, E can be calculated from the slope if all other parameters are known.

Mean volume of droplet of disperse phase is given as below

$$\overline{V} = \frac{V}{n} \tag{11.49}$$

Where V is the total volume of the disperse phase and n is the number of droplets of dispersed phase.

Putting the value of 1/n from equation (11.48) into equation (11.48), we get

$$\overline{V} = V\left[\frac{4}{3}\frac{kT}{\eta}e^{-\frac{E}{kT}}t + c\right]$$

$$\overline{V} = \frac{4}{3}\frac{VkT}{\eta}e^{-\frac{E}{kT}}t + cV$$

Where, cV is the constant value and can be replaced by another constant which is c', we get

$$\overline{V} = \frac{4}{3}\frac{VkT}{\eta}e^{-\frac{E}{RT}}t + c' \qquad (11.50)$$

Differentiating above equation with respect to t, we get

$$\frac{d\overline{V}}{dt} = \frac{4}{3}\frac{VkT}{\eta}e^{-\frac{E}{RT}} \qquad (11.51)$$

This is the rate of coalescence of a phase. Putting value of $A = \frac{4}{3}\frac{VkT}{\eta}$ in equation (11.51), we get

$$\frac{d\overline{V}}{dt} = Ae^{\frac{-E}{RT}}$$

For liquid dispersion phase the value of $\frac{d\overline{V}}{dt} = 10^{-2}A$ (fast rate of aggregation) and for disperse phase the value is 10^{-5}A (slow rate of aggregation).

11.18 STABILITY OF EMULSION

The ability of emulsion to resist coalescence of the droplets of dispersed phase is called the stability of emulsion. Various factors affecting the stability of emulsion have been discussed below

(1) Emulsifier

The emulsions prepared by mixing of two liquids in the absence of emulsifier are unstable. But emulsions in the presence of emulsifier are stable. The stability of emulsion depends upon nature and structure of emulsifier.

(2) Physical Nature of Emulsifier Film

The film formed by an emulsifier acts as a barrier and prevents the aggregation of the droplets of the dispersed phase. Let us take the example of sodium dodecyl sulphate (SDS) that is an anionic surfactant and ionizes as follows

$$H_3C{-}(CH_2)_{11}OSO_3^-Na^+ \rightleftharpoons H_3C{-}(CH_2)_{11}OSO_3^- + Na^+$$

Dodecyl sulphate anion forms an electrical barrier, consisting of negative charges, around the droplet of the dispersed phase as shown in Fig. 11.29. Adjacent droplets repel each other due to the presence of the similar charges on them and hence the emulsion gets stabilized. Sometimes, co-emulsifier is also added to increase the stability of emulsion as it decreases the forces of repulsion between the charges present on the surface of the same droplet. The combination of co-emulsifier with emulsifier increases the mechanical strength of the film.

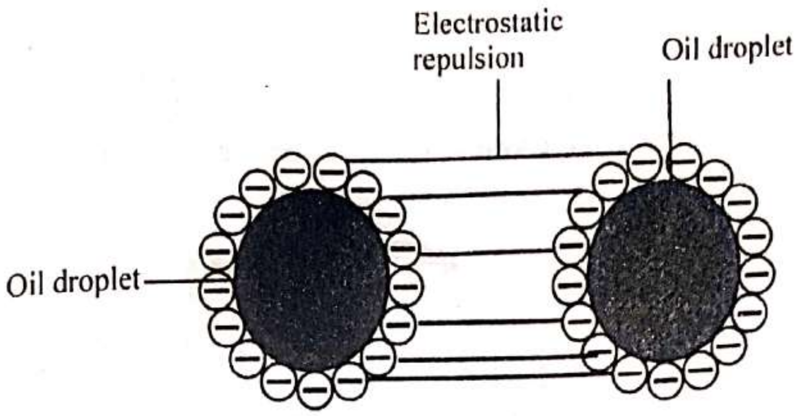


Fig. 11.29 Electrostatic repulsion between charged droplets

(3) Phase Volume Ratio

Varying the volume of the dispersed phase keeping that of the dispersion medium constant, causes a variation in the stability of the emulsion. Increasing the volume of the dispersed phase increases the number of droplets, size of droplets and the viscosity of the emulsion. An increase in the number of droplets and droplet size increases the rate of aggregation and therefore decreases the stability of emulsion. Whereas increase in viscosity, decreases the rate of diffusion hence increases the stability. The maximum permissible volume of the dispersed phase is 74.6% of the total volume. If the volume exceeds this value, phase inversion takes place or emulsion breaking occurs depending upon nature of emulsifier. Concentrated emulsions are more stable than dilute one due to increase of viscosity.

(4) Viscosity

An increase in the viscosity of emulsion decreases the rate of coalescence. Hence the stability of emulsion increases with increase of viscosity. According to Stoke-Einstein formula for spherical droplets, increase in viscosity of dispersion medium decreases diffusion coefficient of the droplets i.e. $D = \frac{k_B T}{6\pi\eta a}$. Some additional substances are added in emulsion to increase the viscosity of continuous phase to get more stable emulsions. These are called thickening agents.

(5) Droplet Size Distribution

Droplet size distribution affects the stability of an emulsion to a great extent. Particles of smaller size gather around the larger one and eventually get submerged into it, losing their own identity. This phenomenon is termed as Ostwald ripening and is prominent in polydispersed emulsions. Hence, monodispersed emulsions are more stable than the polydispersed ones.

(6) Temperature

The rate of coalescence increases exponentially with temperature. An increase in temperature causes an increase in the kinetic energy of the droplets of dispersed phase, due to which diffusion rate increases and as a result, the rate of coalescence also increases. Although the viscosity decreases with temperature but the exponential increase in the rate of coalescence with temperature is dominant.

11.19 BREAKING OF EMULSION (DEMULSIFICATION)

The process of separating the two constituent liquids of emulsion into two layers is called the breaking of emulsion. It is due to the aggregation of the droplets of the dispersed phase and may occur in the form of creaming, sedimentation or coalescence as shown in Fig. 11.30.

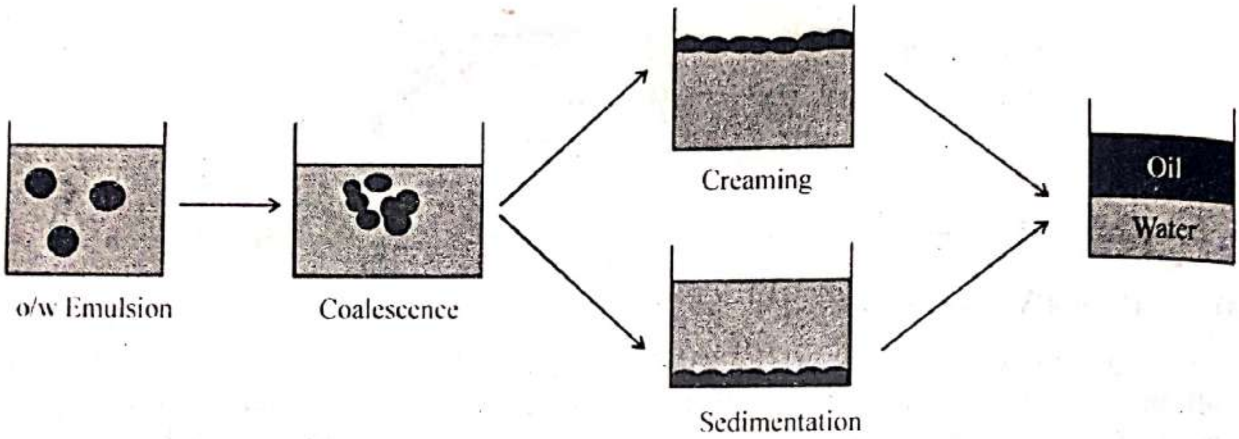


Fig. 11.30 Emulsion breaking by coalescence

Coalescence

When droplets of the dispersed phase aggregate to form a single larger drop, this phenomenon is called as coalescence or coagulation. This coagulation ultimately leads to phase separation. Creaming and sedimentation are two types of coagulation depending upon position of dispersed phase. When the droplets of dispersed phase collect on the surface of emulsion due to small density of dispersed phase, this phenomenon is called as creaming. While sedimentation involves aggregation of droplets of dispersed phase at the bottom of the emulsion due to high density of dispersed phase.

Methods of Demulsification

Some of the methods of demulsification are discussed below

(1) Chemical Method

It involves the addition of an electrolyte to the emulsion that causes aggregation by the removal of charge on the emulsifier and demulsify the emulsion. The quantity of the electrolyte needed to cause aggregation depends upon charge on its cation according to the Hardy Schulze rule.

(2) Mechanical Method

Mechanical methods such as centrifugation or ultrafiltration can be used to separate the two phases present in an emulsion.

(3) Electrical Method

Electrophoresis is one of the frequently used electrical methods for breaking the emulsions in which the charged particles of the emulsifier migrate towards the oppositely charged electrodes and get discharged and precipitated.

(4) Physical Method

Demulsification can also be carried out by heating. Increasing the temperature increases the rate of coalescence, causing the emulsion to become less stable and ultimately break it.

11.20 METHODS OF EMULSION PREPARATION

Emulsification

The process of formation of emulsion by mixing two immiscible liquids with each other in the presence of emulsifier is called emulsification. It involves the breaking of the internal phase into droplets by means of mechanical energy and then stabilizing these droplets in continuous phase with the help of emulsifier.

Methods of emulsification include the conventional as well as advanced methods.

(1) Conventional Methods

The conventional methods usually employed are

(a) Laboratory Method

In this method an organic liquid is stirred with water in the presence of emulsifier for certain period of time to produce an emulsion.

(b) Industrial Method

In this method, dispersed phase and continuous phase along with an emulsifier are sprayed from opposite sides. They mix with each other in the centre to form an emulsion as shown in Fig. 11.31.

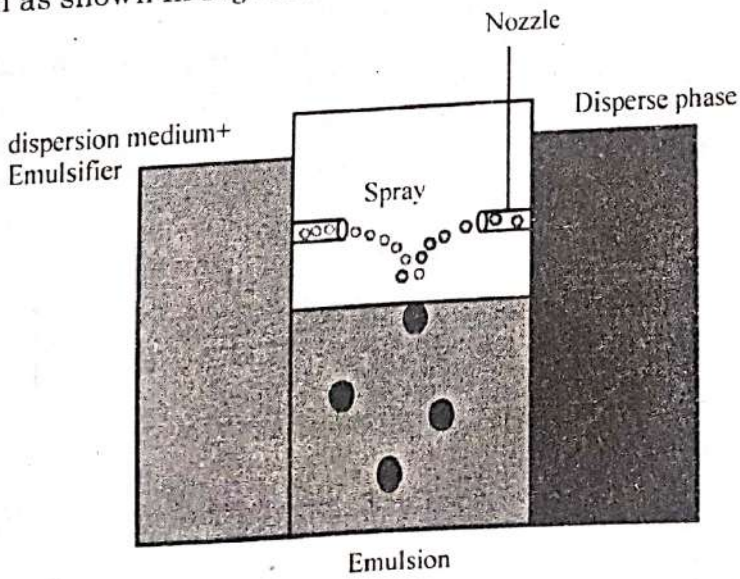


Fig. 11.31 Emulsion preparation on industrial scale by conventional method

(2) Advanced Methods

Membrane emulsification is one of the advanced techniques for preparing emulsions which makes use of a porous membrane. It is further divided into indirect and direct methods.

Indirect Membrane Emulsification Method

In this method, pressure is applied to push the emulsion prepared by classical method through a porous membrane to get a monodisperse emulsion as shown in Fig. 11.32. After passing through the pores of the membrane, the droplets of uniform size are formed.

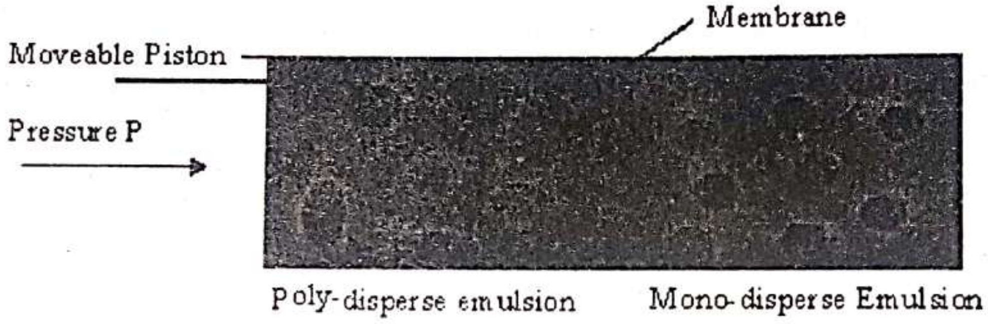


Fig. 11.32 Indirect membrane emulsification method

Direct Method

Direct method includes stirred cell and cross flow methods.

(1) Stirred Cell Method

This method employs a cell containing continuous phase, emulsifier and dispersed phase. The dispersed phase is separated from the continuous phase and emulsifier through a porous membrane. Pressure is applied from the disperse phase liquid side of the cell and the dispersed phase liquid is forced to pass through the porous membrane. Thus dispersed phase enter into the continuous phase where a

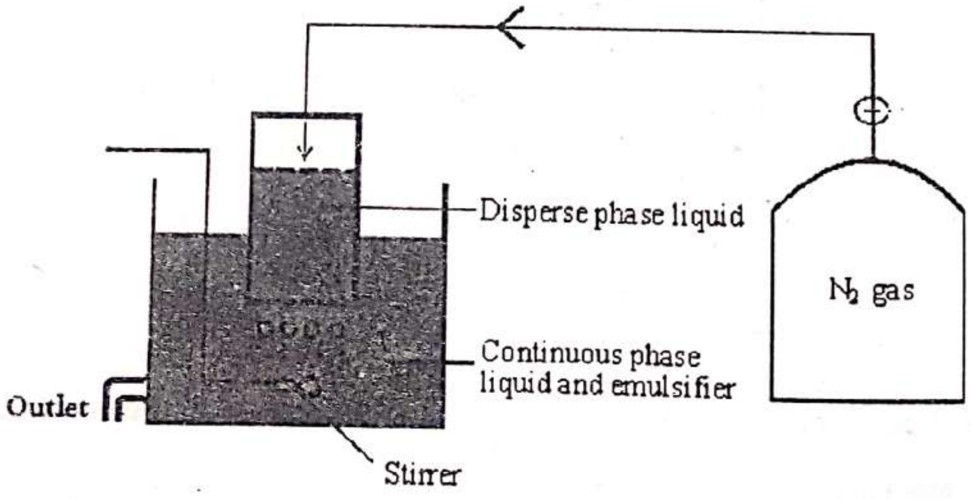


Fig. 11.33 Stirred cell method

stirrer mixes these droplets into the continuous phase in the presence of an emulsifier and the resulting emulsion is passed through an outlet and is collected in a container as shown in Fig. 11.33.

(2) Cross Flow Method

In this method, direction of flow of dispersed phase and continuous phase along with an emulsifier is perpendicular. Thus they mixed with each other perpendicularly to form an emulsion and are collected in separate cells through an outlet as shown in Fig. 11.34. This method employs porous membrane after passing through which small sized droplets of dispersed phase are formed.

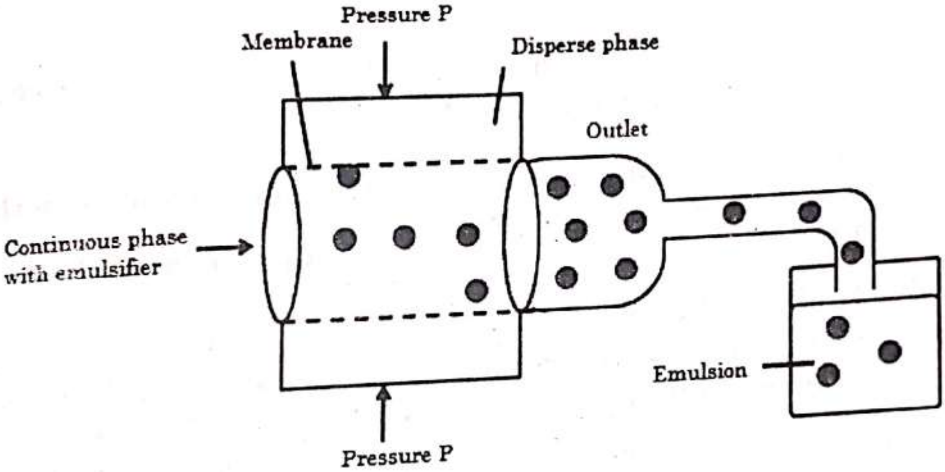


Fig. 11.34 Cross flow method

In this method, the particle size depends on the following factors

(1) Pore Size of Membrane

Particle size is directly related with the pore size of membrane as described by the equation given below

$$\overline{d_d} = \overline{d_p}$$

Where $\overline{d_d}$ and $\overline{d_p}$ represent the average diameter of the droplet and that of the pores of membranes respectively. c is the constant of proportionality. It is a dimensionless quantity and its value depends on the nature of the material of membrane.

(2) Flow Speed of the Continuous Phase

The greater the speed of flow of continuous phase, the smaller will be the size of the particle. Greater speed applies greater force on the droplet to get it released from the membrane pore and small sized droplets are formed.

(3) Pore Density

It is defined as the number of pores per unit area of membrane. High pore density implies that the pores lie very close to each other. Therefore the droplets in the adjacent pores may combine to form larger droplet. A low pore density leads to the formation of small number of droplets. Thus one has to compromise on quantity of droplets to prevent aggregation of droplets.

(4) Pressure

Particle size increases with pressure as high pressure causes greater volume of liquid to come out in lesser period of time.

(5) Pore Distribution

It affects the uniformity of emulsion. If pore distribution is irregular, then polydispersed emulsion is formed and vice versa.

Table 11.3 Difference between conventional and advanced methods

Conventional Method	Advanced Method
1. High energy input is required.	1. Less energy input is required
2. It is difficult to control the droplet size in conventional method.	2. We can control the droplet size in advanced method easily.
3. Non uniform emulsion is formed.	3. Uniform emulsion is formed.
4. The emulsion formed is less stable.	4. More stable emulsion is formed.
5. Droplet size distribution is broad.	5. Droplet size distribution is uniform.
6. Macro level emulsion is produced	6. Micro as well as nano level emulsion can be produced

11.21 APPLICATIONS OF EMULSIONS

(1) Drug Delivery

Drug is hydrophobic in nature and hence not completely soluble in water. The surfactant molecules, after being added, form micelles in the solution and the drug gets entrapped in the core of these micelles. When these micelles enter into the body, they get collapsed at a certain temperature or pH and thus the drug is delivered to the body.

(2) Enhanced Oil Recovery

Three different ways can be employed for oil recovery which include

(i) **Primary oil recovery:** In this method, oil is pumped out of the reservoir through suction pumps. 6 – 15% of the oil is recovered through this method.

(ii) **Secondary oil recovery:** In this method, oil is recovered through flooding. 15 – 30% of the oil is recovered by this method.

(iii) **Tertiary oil recovery:** In this method, oil is recovered through emulsification. An aqueous solution of surfactant is added to the oil reservoir which forms an o/w emulsion. This emulsion is then pumped out through suction pumps. 30 – 60% of oil is recovered by this method.

(3) Emulsions as Microreactors

Emulsions are used as microreactors. For example, when two hydrophilic reactants A and B have been solubilized separately in the presence of a surfactant to give w/o emulsions, the surfactant forms a film around the reactants. If the two emulsions are mixed, then there is an exchange of reactants through collision of water droplets or coagulation of two droplets to form a single droplet as shown in Fig. 11.35. Reactants A and B collide with each other again and again to form product. This cage effect increases the rate of reaction. Recently, metal nanoparticles are prepared using this method. Size of metal nanoparticles can be controlled by controlling size of droplets of emulsion. We can also stabilize metal nanoparticles by this method.

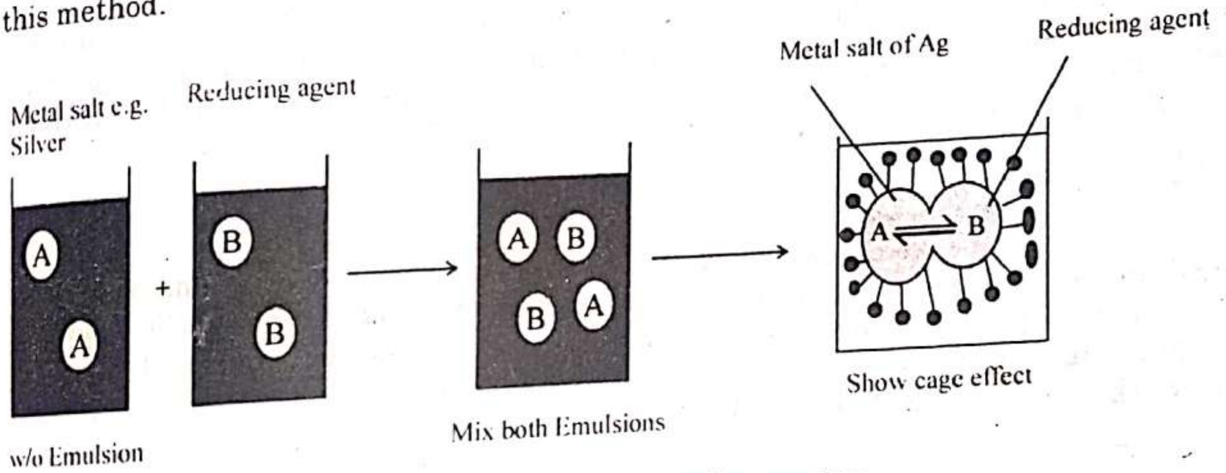


Fig. 11.35 Emulsions as microreactor

(4) Detergents Action

Detergents also work on the principle of emulsification as shown in Fig. 11.36. Surfactant is added to water in order to remove the oil droplets from the cloth, it forms micelles that entrap the oil droplets in hydrophobic core and on the removal of the detergent, oil droplet also gets removed from the surface of the clothes.

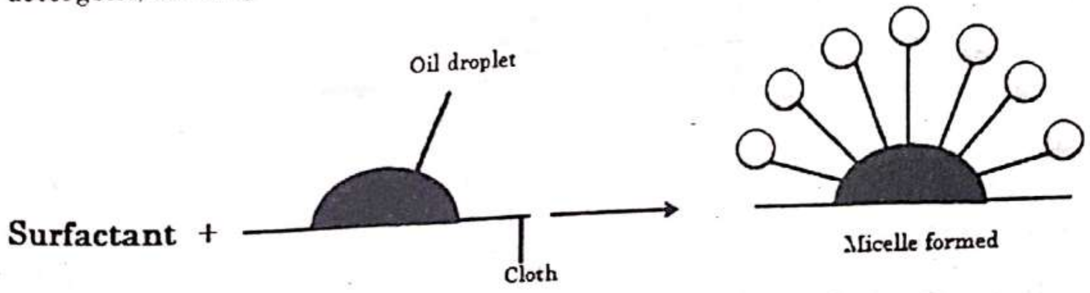


Fig. 11.36 Cleaning action of soap

(5) Food Industry

Food industry also makes use of the process of emulsification. For example, milk is an emulsion which is stabilized by an emulsifier named casein. The food we cook is usually an emulsion containing oil, water and a variety of sausages. Likewise, the process of baking also involves the addition of an emulsifier named as diacetyl tartaric (acid) ester of monoglycerides and abbreviated as DATEM.

(6) Cosmetic Industry

Many different emulsifiers are used in cosmetics to prepare emulsions such as cream or lotion etc. which help them to spread and get absorbed or adsorbed by the skin, because skin also has hydrophillic and hydrophobic dual nature. Common examples of emulsifiers used in cosmetic industry include emulsifying wax, cetyl alcohol, poly sorbate 20 (Tween 20).

(7) Froth Flotation Process

In metallurgical process, w/o emulsions are used to concentrate the ore by froth flotation process which is based on emulsification. The stirring of ore containing w/o emulsion causes foaming which is skimmed out and used for further metallurgical processes.

11.22 GELS

A gel is a colloidal system in which dispersed phase is liquid and dispersion medium is solid. It is a two phase system, one is continuous phase that is solid and second is dispersed phase that is liquid. So it is semi-solid material. Dispersion medium in gels is solid and has a specific structure i.e. cross-linked polymeric network system as shown in Fig. 11.37.

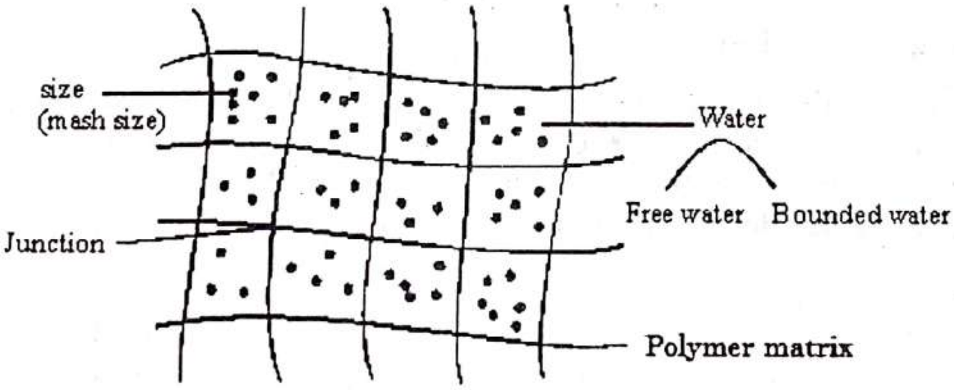


Fig. 11.37 Structure of gel

Structure of Gels

It is a two phase colloidal system in which continuous phase is solid material which may be branched or cross-linked polymer system. While, discontinuous phase is liquid and if this liquid is water it is called hydrogel. In case of hydrogels the water entrapped in the network may be of three types.

(1) **Primary bound water:** Water bound to polymer network through hydrogen bonding.

(2) **Secondary bound water:** Water bound to polymer through hydrophobic interactions (Vander Waal forces). Primary and secondary bound water called total bound water.

(3) **Free water:** Water that can freely enter or leave the network all the time is called free water.

Classification of Gel

On different basis, gels can be classified as listed below

(1) On the Basis of the Size of Polymer Matrix or Dispersion Medium

On the basis of size of polymer matrix, gel is divided into three types as shown in Fig. 11.38. If particle size of gel is very large then gel system is called macro gels. If particle size of gel is in range of 0.1-1 μm, then gel system is called micro gels and if particle size of gel is in range of 1-100 nm then gel system is called nano gels.

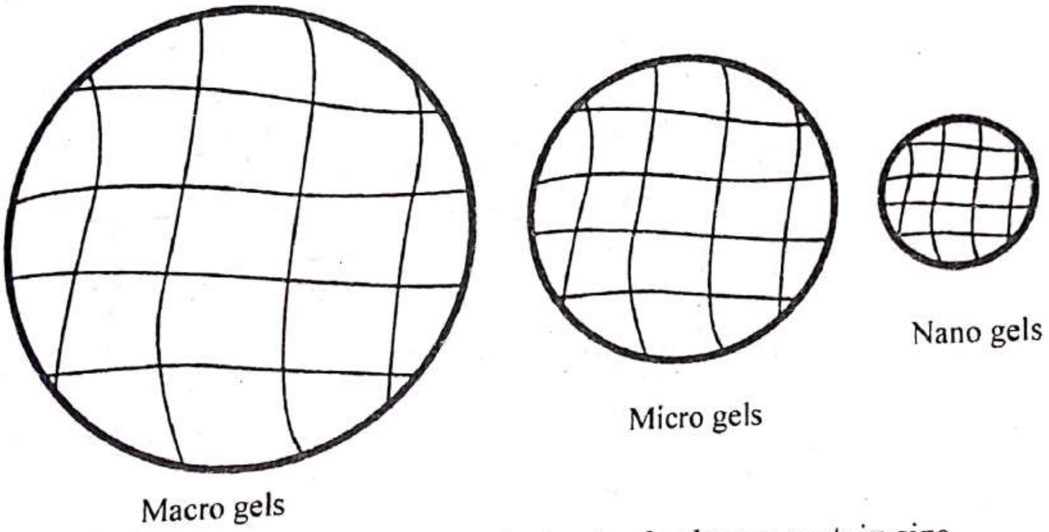


Fig. 11.38 Classification on the basis of polymer matrix size

(2) On the Basis of Nature of Dispersion Medium

If network is made up of organic polymer then gel system is called organo gel and if it is made up of inorganic polymer (silicone or silica etc) then gel system is called inorganic gel.

(3) On the Basis of Disperse Liquid

If water is entrapped in the network then gel is called hydrogel. If benzene is entrapped in the network then gel is called benzogel. Similarly, if alcohol is entrapped in the network then gel is called alcogels.

(4) On the Basis of Nature of Cross-Linkage

On the basis of cross-linkage gels are divided into two types.

(a) Physically cross-linked gels are such gels in which vander waal's forces are present in the network.

(b) Chemically cross-linked gels possess chemical bonding is present in the network.

(5) On the Basis of Physical Properties

On the basis of elasticity, the hydrogels can be classified as

(a) Elastic

(b) Nonelastic

"The gels from which liquid can be removed and can be added again with reversible size variation of gel particle are called elastic gels". These are also known as reversible hydrogels as shown in Fig. 11.39.

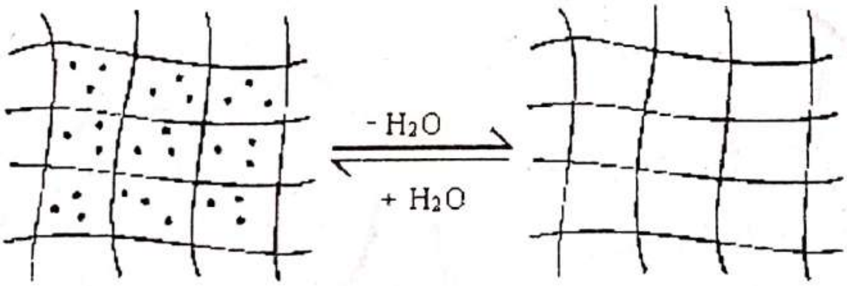


Fig. 11.39 Elastic or reversible hydrogel

"The gels from which liquid can be removed from the network but cannot be added again to the gel network are called non elastic gels" as shown in Fig. 11.40. Most of the gels have elastic properties. The elasticity depends upon cross-linking density. By increasing cross-linking density, elasticity decreases. Elastic gels can swell or shrink with change in conditions like temperature, ionic strength and pH of the medium.

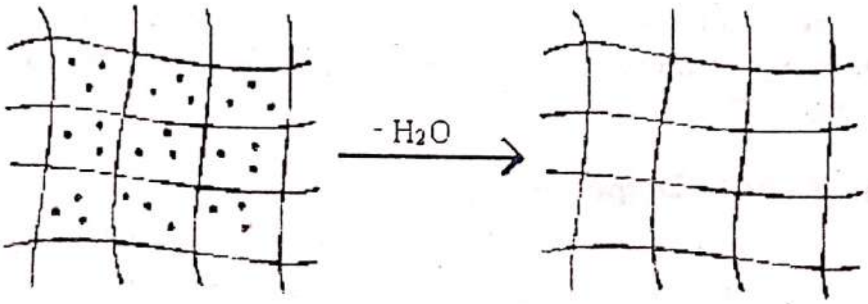


Fig. 11.40 Non elastic gel

(6) On the Basis of Amount of Dispersed Phase (Liquid-Solid Network)

If liquid or dispersed phase in gel is 95% or more then gel is called jelly. If liquid or dispersed phase in gel is less than 95% then gel is called simple gel. Xerogels can be obtained by removal of liquid from the gel network but liquid cannot be removed completely from gels. Aero-gels are obtained by replacing liquid with air.

(7) On the Basis of Responsive Behavior

(a) Responsive Gels

Responsive gels swell or deswell in response to one or more slight changes in the environment and are therefore called 'smart' materials. It is also called stimuli responsive gel because they show sudden change in their physical structure on applying external stimulus. The external stimulus may be

(a) pH
(b) Temperature
(c) Ionic strength
(d) Electric field
(e) Intensity of light

Fig. 11.41 illustrates that at low temperature gel is in swollen form but with the increase in temperature gel shrinks due to the expulsion of water from the gel network.

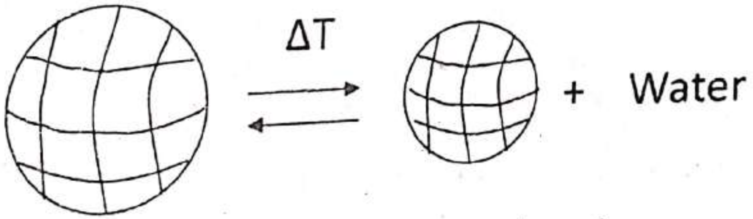


Fig. 11.41 Stimuli responsive gel

(b) Non-Responsive Gels

Non-responsive gels simply swell upon absorption of water. These gels do not show any variation in size with change in environmental stimuli.

(8) On the Basis of Stimuli

On the basis of stimuli, responsive gels can be classified as

(a) Temperature sensitive gels
(b) Electric field sensitive gels
(c) Glucose sensitive gels
(d) Ionic strength sensitive gels etc.

(9) On the Basis of Morphology

On the basis of morphology, gels can be classified as

(a) Homogenous gels

(b) Non-homogenous gels

(10) On the Basis of Additional Material

Mostly microgels contain some additional material like nanoparticles. Such microgels which possess nanoparticles are called hybrid microgels. Hybrid microgels can be classified as

(a) Microgels covered with nanoparticles

(b) Microgels filled with nanoparticles

(c) Core-shell hybrid microgels

11.23 METHODS FOR THE PREPARATION OF GELS

"The process of formation of gel by cross-linkage is called gelation". Some methods which are used for the preparation of gels are discussed below.

(1) By Coagulation Method

When solid particles are dispersed in liquid a sol system is formed. When coagulating agent (like electrolyte) is added in this sol, particles will coagulate to form a solid network and liquid is entrapped in it (Fig. 11.42). The process of conversion of sol into gel is called sol-gel transformation. During this process, physical properties get change. For example, viscosity of the system increases when system moves from sol to gel. A certain value of concentration of sol is required for transformation of sol into gel. That minimum value of sol concentration at which transformation occurs is called critical concentration.

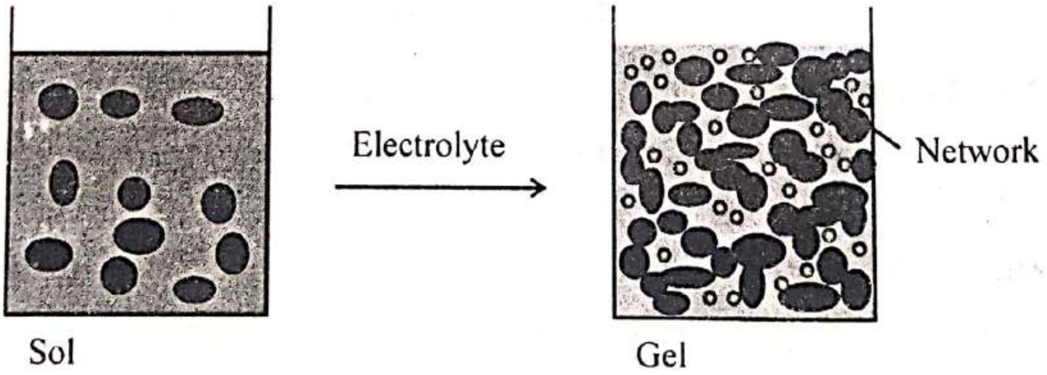


Fig. 11.42 Transformation of sol into gel

(2) By Chemical Reaction

Gel can be made by chemical reaction e.g. if two reactants A and B react with each other and two products formed are one is soluble and other is insoluble.

$$A + B \rightarrow C + D$$

Here C is insoluble product. Insoluble particle or product form sol and then aggregate to form gel at certain concentration of sol. For example

$$\underset{\substack{\text{Barium}\\ \text{thiocyanate}}}{BaSCN} + \underset{\substack{\text{Mangnese}\\ \text{sulfate}}}{MnSO_4} \rightarrow \underset{\substack{\text{Barium}\\ \text{sulfate}}}{BaSO_4} + \underset{\substack{\text{Mangnese}\\ \text{thiocyanate}}}{MnSCN}$$

Here barium sulfate is water insoluble.

(3) Cooling of the Colloidal System

When colloidal system is cooled then it becomes inter-linked or cross-linked and gel is formed.

(4) Solvent Exchange

In this method one liquid in a sol is replaced with another one. If the stability of sol particles in liquid B is lower than the stability of sol in liquid A, then sol particles combine to form a crosslinked network in liquid B and gel is formed.

(5) Gelation Caused by Combination of Oppositely Charged Polyelectrolyte

Polyelectrolyte molecule may contain many ionizable pendant groups like carboxylic group (–COOH) on one chain. When -COOH ionizes, negative charge is produced on the chain. If another chain contains such group e.g. amino group that produces positive charge on the chain on protonation (Fig. 11.43). Then negative and positive charges attract each other by electrostatic force of attraction and gets aggregate to form gel.

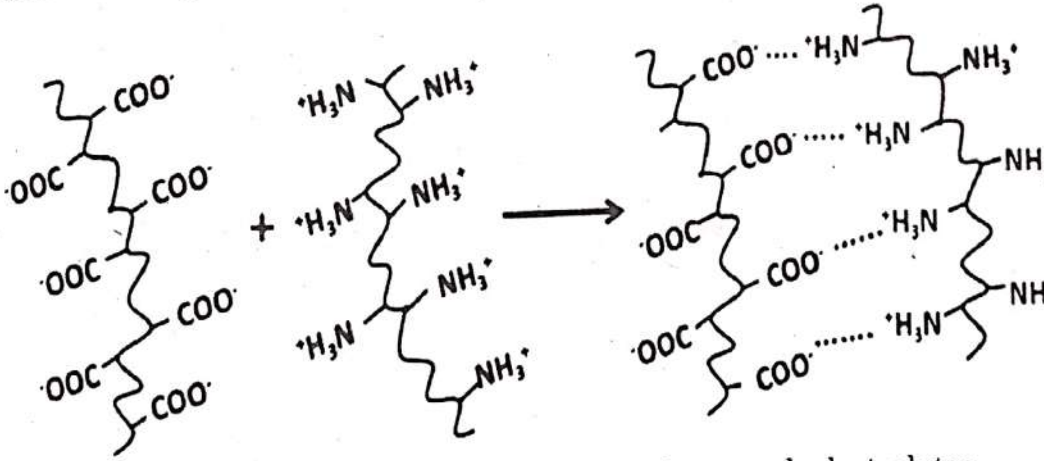


Fig. 11.43 Gel formation by oppositely charge polyelectrolytes

(6) Intra-molecular Hydrogen Bonding

Gel is also formed by intra-molecular hydrogen bonding in a molecule. In this way a large molecule is converted into cross-linked network by self bonding as shown in Fig. 11.44.

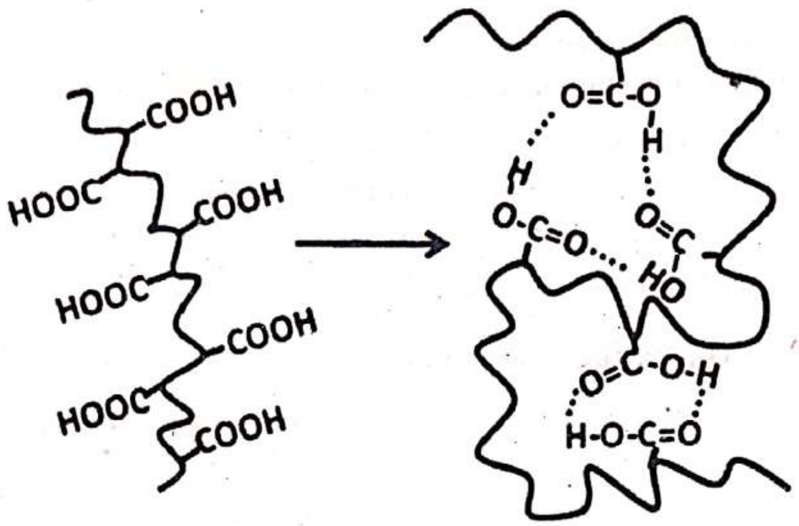


Fig. 11.44 Gel formed through intra-molecular hydrogen bonding

(7) Heating

When miceller solution is heated, micelles interlink with each other to form physical gel. The gelation in miceller solution of block copolymers of oxyethylene and oxybutylene at high temperature is an example of gel formation on heating.

11.24 PROPERTIES OF GELS

(1) Thixotropy

After a long standing time, dispersed phase of sol change into dispersion medium and dispersion medium changes into disperse phase to form gel and after shaking it again convert into sol as shown in Fig. 11.45. This property of sol-gel reversible transformation is called thixotropy.

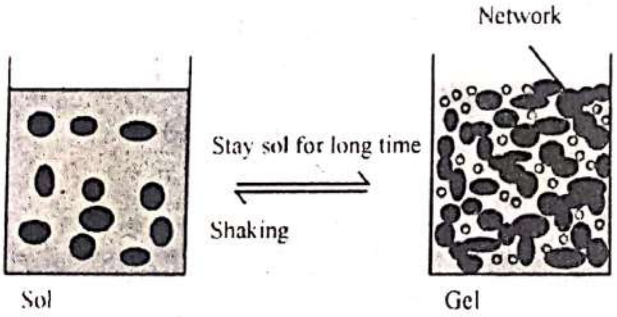


Fig. 11.45 Sol-gel transformation

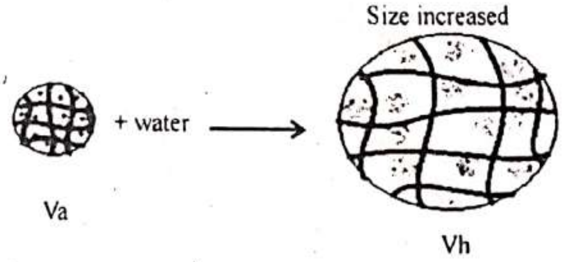


Fig. 11.46 Swelling of gel

(2) Swelling

When gel is soaked in water, then size of gel particles increases and swelling occurs as shown in Fig. 11.46.

But different forces act on it such as

(a) Osmotic pressure

(b) Cross-linking force resisting the swelling

At the stage of equilibrium

Cross-linking force = Osmotic pressure

The extent of swelling is measured in terms of swelling ratio which can be written as

$$\alpha = \frac{V_h}{V_a}$$

Where, V_h is the volume of hydrated particle in swollen state and V_a is the volume of gel particle in shrunken state.

If particle is spherical then $V_h = \frac{4}{3}\pi R_h^3$

And $V_a = \frac{4}{3}\pi R_a^3$

So, we get $\alpha = \left(\frac{R_h}{R_a}\right)^3$

If the value of α is high then the swelling ability will be higher. Rate of swelling depends upon the gel particle size if size is small then rate of swelling is high and vice-versa.

(3) De-swelling

(a) Shrinking

When water is removed from gel through some external force then size of the gel will reduce called shrinking of the gel.

(b) Syneresis

Gel undergoes a shrinkage in volume on standing in open atmosphere with the spontaneous evaporation of water is called syneresis.

(4) Responsive Behavior

Consider an example of poly(N-isopropylacrylamide) [p(NIPAM)] having coil conformation. When heat is supplied it changes its conformation from coil to globule form. The temperature-induced coil to globule transition of p(NIPAM) is shown in Fig. 11.47. The temperature at which this transition occurs is called the lower critical solution temperature (LCST).

This effect can be explained on the basis of structure of p(NIPAM) that is shown in Fig. 11.48. At low temperatures, p(NIPAM) is highly solvated due to hydrogen bonding between the amide groups on the polymer chain and the water molecules. At elevated temperatures, the hydrogen bonds between the polymer and the water molecules are broken, and intra-molecular hydrogen bonds between the C=O and N–H groups are generated leading to removal of water from the interior of polymer network. Consequently the polymer-polymer interactions become stronger than the polymer-solvent interactions at higher temperature, so polymer attains conformation of a globule.

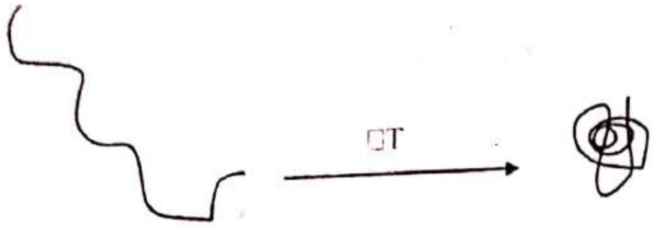


Fig. 11.47 Coil to globule transformation in p(NIPAM)

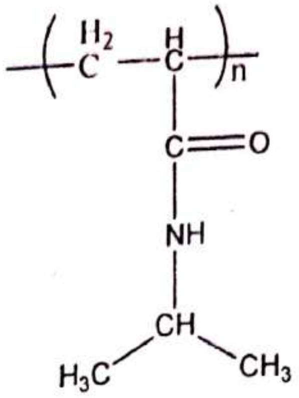


Fig. 11.48 Structure of p(NIPAM) chain

(a) Temperature Sensitivity

Such gels which show swelling or de-swelling in response to change in temperature are called thermo sensitive gels as shown in Fig. 11.50.

Thermo responsive behavior of microgels can be explained on the basis of change in hydrodynamic radius of gel particle with change in temperature. The value of hydrodynamic radius as a function of temperature for p(NIPAM) microgels as shown in Fig. 11.50. The hydrodynamic radius decreases with increase of temperature. The value of temperature at which rate of change of hydrodynamic radius with respect to temperature is maximum is called volume phase transition (VPTT). VPTT of a microgel is a function of cross-linking density and hydrophilic and hydrophobic groups present in gel network. The value of VPTT can be measured from plot of hydrodynamic radius versus temperature as shown in Fig. 11.51.

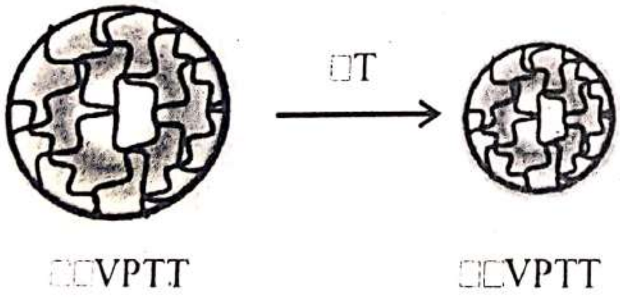


Fig. 11.50 Pictorial diagram showing temperature sensitivity of gels

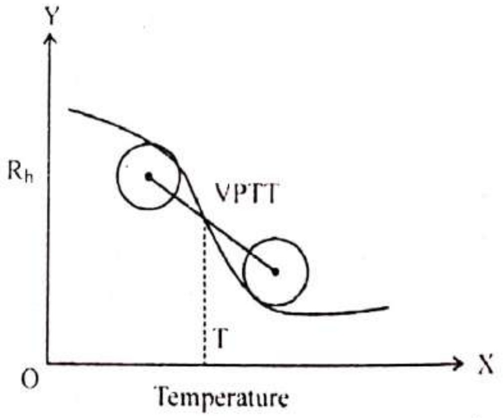


Fig. 11.51 Determination of VPTT

(b) pH Sensitivity

The cross-linked polymer microgel particles which swell or deswell when the pH approaches the pK_a/pK_b of the functional monomer incorporated inside the particles are called pH sensitive gel. The carboxylic groups become ionized with the increase in pH by adding base as shown in Fig. 11.52. As a result gel size increases due to electrostatic repulsion between similarly charged groups present in network. Increase in size decreases water potential in gel. So water molecules move from medium into gel, resultantly particle size increases. Thus electrostatic repulsion and water content, both play role in increasing size of gel.

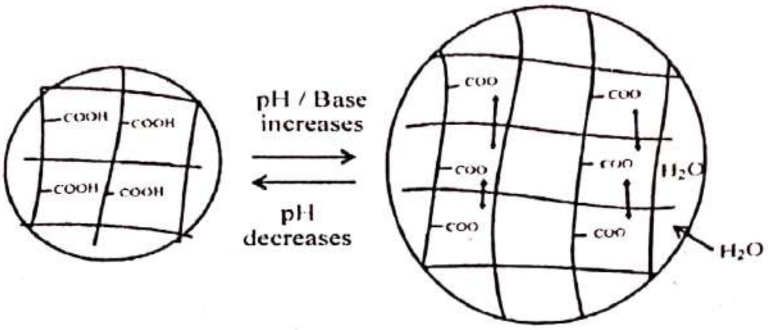


Fig. 11.52 Swelling–deswelling in pH responsive microgels

(c) Glucose Sensitivity

The microgels which respond to the variations in glucose concentration by swelling or shrinking are called glucose-responsive microgels. Such smart microgels are used for quantitative analysis of glucose in complex physiological mixtures as well as for drug delivery, especially delivery of insulin for diabetic patients.

11.25 APPLICATIONS OF GELS

(1) Drug Delivery

One of the application of gels is controlled drug delivery. The open network structure of microgels can be used to incorporate small molecules such as drugs in their interiors while their large sensitive swelling-deswelling transitions may be employed as physical and chemical triggers to direct the release of the drugs as shown in Fig. 11.53. Drug delivery depends upon the responsive behavior of gel.

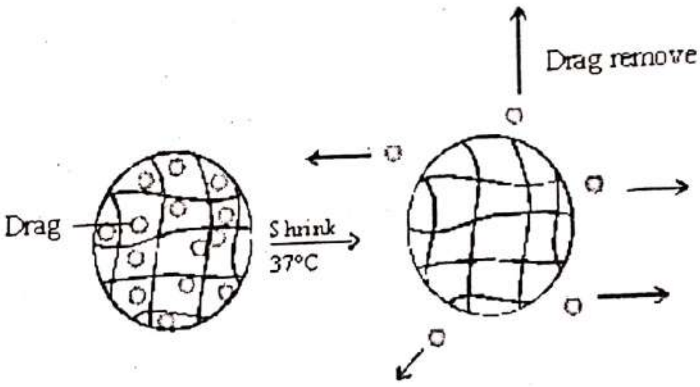


Fig. 11.53 Drug delivery

(2) Hybrid Microgels in Nanotechnology

Microgels find extensive applications in the field of nanotechnology. Microgels are used as microreactors for synthesis of different types of inorganic nanoparticles of fascinating properties and applications. Hybrid microgels are well known for their catalytic applications.

(3) Microgels in Coating Industry

Microgels play important role in improving rheological properties of paint and performance of films. That is why they are extensively used in coating industry

They impart shock resistance to the films owing to their flexible sponge-like structures.

(4) Microgels in Heterogeneous Catalysis

Recently, metal nanoparticles containing microgels have been attained a lot of attention to scientists working in the field of catalysis due to stability, durability of catalyst and open circuit for reactant diffusion to the catalyst. The catalyst can be recovered for re-use. Reduction of p-nitrophenol to p-aminophenol is widely used to study the catalytic activity of hybrid microgels. The kinetics of this reaction in the presence of hybrid microgel can be easily monitored by UV-Visible spectroscopy. p-nitrophenol in slightly basic medium absorbs at 400 nm. During the progress of reaction absorbance decreases at 400 nm due to consumption of p-nitrophenol and absorbance at 300 nm concomitantly increases with the passage of time due to increase of concentration of p-aminophenol (Fig. 11.54). Mathematical treatment of the kinetics of catalysis is given below

Let, p-nitrophenol = A, sodium borohydride = B and p-aminophenol = P

$$\begin{array}{lcccccc} & A & + & B & \longrightarrow & P \\ t = 0 & c_o & & b_o & & 0 \\ t = t & c & & b_o - x \approx b_o & & x \end{array}$$

The concentration of B is taken in excess therefore, $b_0 - x \approx 0$ so,

$$-\frac{dc}{dt} \propto c$$

$$-\frac{dc}{dt} = k_{app}c$$

By separating variables and integrating above equation will be

$$-\int \frac{dc}{c} = k_{app} \int dt$$

$$-\ln c = k_{app}t + \text{constant} \qquad (11.52)$$

When t = 0, then $c = c_0$, by putting this approximation on above equation, we get

$$-\ln c_o = \text{constant}$$

By putting value of constant in equation (11.52), we get

$$-\ln c = k_{app}t - \ln c_o$$

$$\ln c_o - \ln c = k_{app}t$$

$$\ln\left(\frac{c_o}{c}\right) = k_{app}t \qquad (11.53)$$

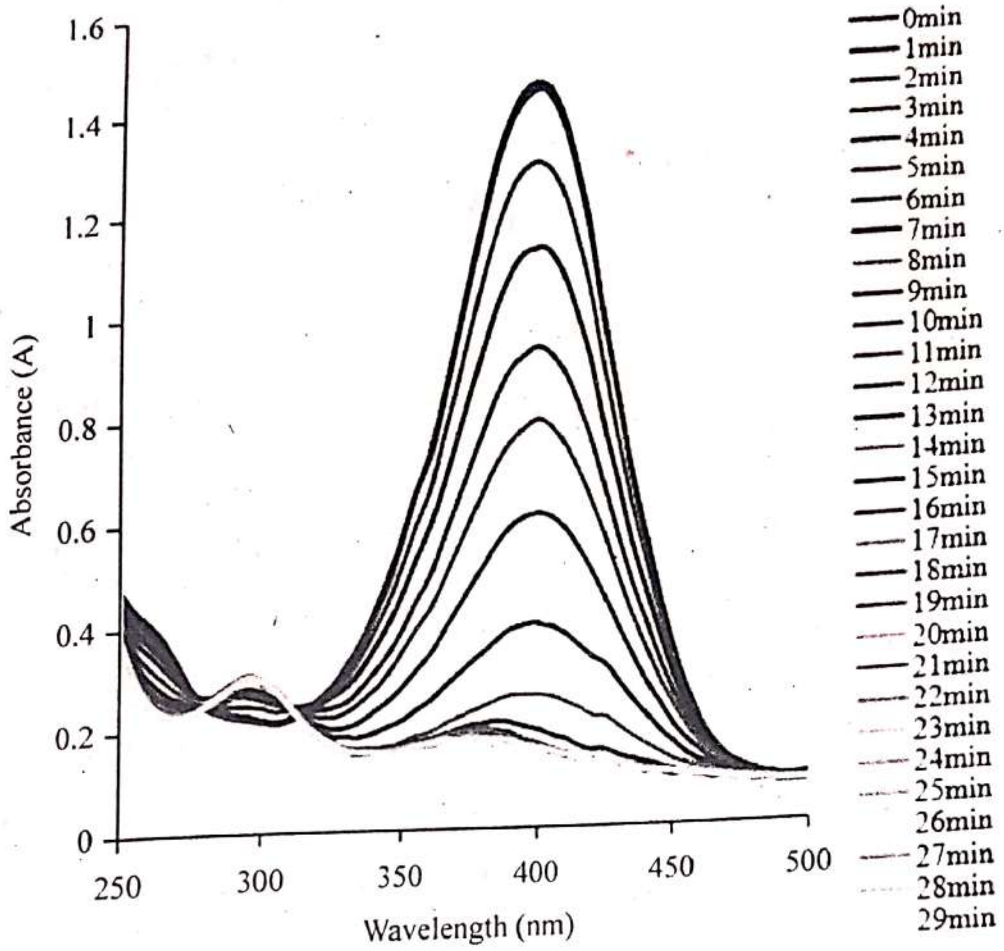


Fig. 11.54 UV-Visible spectrum of catalytic reduction of p-nitrophenol

Since,

$$A_o = \varepsilon c_o l \tag{11.54}$$

$$A_t = \varepsilon c_t l \tag{11.55}$$

By dividing equation (11.54) by equation (11.55), we get

$$\frac{c_o}{c_t} = \frac{A_o}{A_t}$$

By replacing the c_o/c in equation (11.53) by A_o/A_t, we get

$$\ln\left(\frac{A_o}{A_t}\right) = k_{app}t$$

$$\ln\left(\frac{A_t}{A_o}\right) = -k_{app}t \tag{11.56}$$

This is an equation of straight line with slope $-k_{app}$. So, by plotting a graph of $\ln(A_t/A_o)$ versus t we can determine the apparent rate constant (k_{app}) from the slope.

11.4 Difference between emulsions and gels

Emulsions/Emulgents	Gels
1. Phases	
Dispersed phase as well as dispersion medium, both are liquids.	Dispersed phase is liquid while dispersion medium is solid.
2. Volume Percentage of Phases	
Maximum volume percentage of dispersed phase for a stable emulsion is 74.6 %. Molecules of dispersed phase are closely packed when their percentage in emulsion is 74.6 %.	Maximum volume percentage of dispersed phase in stable gels is 99.9 %. At this condition, dispersion medium constitutes only 0.1 % of total volume.
3. Physical Appearance	
Appearance of emulsions is similar to liquids.	Gels are versatile in physical appearance. They can be solid, liquid or semi-solid.
4. Emulsifier	
Emulsifier is added to decrease surface tension between dispersed phase and dispersion medium.	No emulsifier is added to decrease surface tension between dispersed phase and dispersion medium. However surfactant is added only to increase stability of microgel particles in solvent.
5. Crosslinker	
No crosslinker is added.	Crosslinker is added to form crosslinked network by dispersion medium. Crosslinked network is more stable.
6. Thixotropy	
Emulsions do not show thixotropic behavior.	Thixotropy is a property of gels. They can easily undergo sol and gel inter-transformations.
7. Coalescence	
Coalescence occurs easily in emulgents.	Gels get aggregate only under some specific conditions of pH, temperature, ionic strength etc.
8. Breaking	
Emulsions can be easily and completely broken into their components.	100 % breaking of gels into their components is not possible. Moreover breaking of gels is not easy. components.
9. Elasiticity	
Emulsions are not elastic.	Gels show good elasticity.
10. Preparation Methods	
Physical and chemical methods are used to prepare emulsions.	Chemical methods are used to prepare gels.

Emulsions/Emulgents	Gels
11. Classification	
Emulsions can be classified on the basis of position of inner and outer phase i.e.; o/w and w/o emulsions.	Gels cannot be classified in this way. Rather they can be classified on the basis of nature of inner and outer phases i.e.; organogels, benzogels etc.
12. Mutiple Presence of Phases	
Multiple emulsions exist i.e.; o/w/o or w/o/w emulsions.	No multiple gel exist.
13. Syneresis	
Emulsions do not show syneresis.	Gels show syneresis.
14. Examples	
Crude oil.	P(NIPAM) microgel.

QUESTIONS

Q.1. How will you classify gels? Explain their structure. Give methods for preparation of gels and Emulsions.

Q.2. How will you differentiate between gels and emulsions? Explain the methods of breaking of emulsions.

Q.3. What are emulsions? How are they prepared? Give their properties.

Q.4. Write a short note on the orientation theory of emulsification and wetting and emulsification.

Q.5. Define CMC and derive the relation between free energy of micellization and CMC for non ionic surfactant system.

Q.6. The CMC value of $E_{20}B_{10}E_{20}$ at 25°C in aqueous medium is 6.2×10^{-2}mM. Calculate the free energy of micellization. (−24 kJ/mol)

Q.7. Micellization of block copolymer in aqueous medium is important in industrial processes. Thermodynamics of micelization of such kind of block copolymers of oxybutylene and oxyethylene was investigated by Farooqi and his coworkers [Journal of dispersion Science and Technology 34(2013), 400] by monitoring $\ln X_{cmc}$ versus 1/T using surface tension measurements. Following data were obtained at 293K

Surfactant	ΔG_{mic} (kJ/mol)	ΔH_{mic} (kJ/mol)
$E_{20}B_{10}E_{20}$	-24.55	42.204
$E_{30}B_{10}E_{30}$	-17.338	28.849
$E_{48}B_{10}E_{48}$	-17.057	17.976

(i) Calculate $T\Delta S_{mix}$

(ii) Compare association process of the block copolymers in the light of given values of thermodynamic parameters.

Q.8. Explain role of various factors in determination of stability of an emulsion by using explanation of quantitative theories.

Q.9. How can you differentiate oil in water and water in oil emulsions?

Q.10. Explain the role of hybrid microgels in catalysis using a suitable model reaction.

Q.11. Briefly discuss the smart behavior of microgels with respect to temperature and pH change in the environment.

Q.12. Write a note on membrane emulsification. How can you control the droplet size by membrane emulsification?

Q.13. How can you use Dynamic Light Scattering and tensiometry to study the parameters of micellization?

Q.14. What are surfactants? How can you classify surfactants? Discuss role of surfactants as emulsifier in emulsification.

Q.15. How can you determine size of droplets of an emulsion using sedimentation method?

Q.16. What is CMC? Give two methods for determination of CMC of a surfactant.

REFERENCES

1. Glasstone, S. 1995. Physical Chemistry, Macmillan and Co. Ltd. St. Marlins Street, London.
2. Maron, S.H. and C.F. Prutton, 1965. Principles of Physical Chemistry, The Macmillan Company, Collier Macmillan Ltd. London.
3. Birdi, K. S. 1997. Hand book of Surface and Colloid Chemistry, CRC Press, New York.
4. Rosen, M. J. 1978. Surfactants and Interfacial Phenomena, John Wiley, New York.
5. Kundu S. and S.K. Jain. 2001. Physical Chemistry, S. Chand and Co (Pvt) Ltd, New Delhi.
6. Levine, I.N. 2005. Physical Chemistry, Total McGraw Hill Eduction Pvt Ltd., New Delhi, India.
7. Silbey, R. J. Alberty, R. A. and M. G. Bawendi 2005. Physical chemistry, Wiley, India.
8. Remann, K.V. 1990. Group Theory and its Applications to Chemistry. Data McGranOHil Publishing (O), New Delhi.

Chapter 12

PHOTOCHEMISTRY

12.1 INTRODUCTION

Photochemistry is the branch of chemistry which deals with the study of chemical reactions produced directly or indirectly by the radiation lying between visible and ultraviolet (800—200 nm) region of electromagnetic spectrum. It deals with the study of effect of radiant energy on chemical reactions, the rate and the mechanism by which the reactions are either initiated or affected by light radiation. It also includes the study of reverse reactions in which the chemical energy released is emitted as light. Reactions which occur with the absorption or emission of light are called *photochemical reactions.* There are so many reactions which occur due to absorption of light radiations by matter. These reactions may be of any type like synthesis, decomposition, isomerization, oxidation-reduction and polymerization.

Ordinary or thermal reactions are initiated by activation brought about through molecular collisions. Such reactions can occur only when these are accompanied by a decrease in free energy. If increase in free energy is involved, no reaction is possible. However, thermal activation is not the only means by which the energy of atoms or molecules can be raised sufficiently to cause reaction. Another way to raise the energy of activation of atoms or molecules is to bring the reactant molecules into collision with light quanta of electromagnetic radiation, e.g. UV-visible, gamma rays, X-rays etc. In fact with the absorption of such a large quanta of radiation, a molecule may be ruptured. Such absorption of light by an atom or molecule leads to its excitation, and if the activation is sufficiently great, chemical reaction may result. In this way absorbed light can affect the rate of a chemical reaction and frequently bring about chemical changes under conditions where thermal activation alone would not be affective. Thus, photochemistry comprises the study of chemical reactions produced directly or indirectly by light. The term light is used in a wide sense and includes all radiations. In general, visible and ultraviolet light is photochemical active, while infrared light has practically no effect on the chemical reactions. On the other hand, if high energy photon from X-rays or gamma-rays be used, innumerable molecules coming in their path would be ionized. This ionization would lead to chemical changes through secondary processes. The study of effects of these radiations therefore, comprises the subject matter of *Radiation Chemistry*. For example a mixture of hydrogen and chlorine remain unchanged with the lapse of time but when it is exposed to light, a reaction occurs with a loud explosion. The reaction of carbon dioxide (CO_2) and water (H_2O) in the presence of chlorophyll is a photochemical reaction. The vision process involves the absorption of photon by visual pigment rhodopsin. The chemical reactions occurring in atmosphere are photochemical reactions. For example formation and decomposition of ozone in stratosphere is a very important reaction for life on earth. The photo-polymerization is commonly used technique for synthesis of many synthetic polymers. Kinetics of chemical reactions has been investigated using techniques based on photochemistry. For example flash photolysis is used to identify the short lived species generated in a chemical reaction. The use of techniques based photochemistry is increasing day by day in nuclear research, inorganic estimation, food research, qualitative and quantitative analysis and medicinal research. This chapter deals with study of laws of photochemistry, kinetics of photochemical reactions, photochemical process like fluorescence and phosphorescence, chemiluminescence and lasers. The mechanisms involved in photosensitized reactions have been also described in this chapter.

12.2 PHOTOCHEMICAL AND THERMAL REACTIONS

The chemical reactions are results of collision of reactants. Each collision cannot cause a chemical reaction but a fraction of collision with proper orientation and sufficient energy causes a chemical reaction. The minimum energy needed to convert reactants into product is called *activation energy*. This energy can be provided by heating or irradiating reactions. Therefore chemical reactions can be classified as thermal and photochemical reaction. The basic differences between these reactions are given in Table 12.1.

Table 12.1 Distinguishing properties between thermal and photochemical reactions

Thermal reactions	Photochemical reactions
These reactions involve absorption or evolution of heat energy.	These chemical reactions evolve absorption/emission of light energy.
These reactions may occur in the absence of light.	These reactions take place in the presence of light only.
Temperature significantly affects the rate of thermal reactions.	Temperature has very little effect on photochemical reactions.
These reactions are not affected by light intensity.	Light intensity significantly affects the rate of reaction.
The free energy change of thermal reaction is always negative.	Free energy of photochemical reaction may be negative or positive.
These reactions are accelerated by catalysts.	Some photochemical reactions involve photosensitizers instead of catalyst.
Example: Production of ammonia in Haber's process is an example of thermal process.	Example: A mixture of hydrogen and chlorine remain un-reacted in the absence of light. This reaction takes place only in the presence of light.

12.3 LIGHT ABSORPTION AND LAWS OF ABSORPTION

When a solution or medium is irradiated with light, a part of it is absorbed. This light absorbed by the medium molecules causes a photochemical reaction. The absorption of monochromatic radiation by homogeneous solution or system is explained on the basis of two empirical laws i.e. Lambert's law and Beer's law. Both these laws are valid for monochromatic radiations passing through homogeneous medium.

12.3.1 Lambert's law

A relationship between the amount of light absorbed and thickness of the homogeneous absorbing medium was given by Lambert in 1758. It is an empirical relation and known as Lambert's law. This law is stated as "when a monochromatic beam of light passes through a homogeneous transparent medium, the rate of decrease of intensity of light with respect to the thickness of the medium is directly proportional to the intensity of light".

Mathematically Lambert's law can be written as

$$-\frac{dI}{dl}\alpha I$$

Where I is the intensity of light at any thickness l and –dI/dl is the rate of decrease of intensity of light with respect to thickness of the homogeneous medium. By rearranging the above expression, we get

$$-\frac{dI}{I}\alpha dl$$

Or

$$-\frac{dI}{I}=kdl \qquad (12.1)$$

Where k is the proportionality constant and it is called absorption co-efficient. Its value depends upon the nature of the absorbing medium. Its SI units are m^{-1}. Equation (12.1) is variable separable 1st order differential equation. It can be integrated by separating variables as

$$\int\frac{dI}{I}=-k\int dl$$

$$\ln I=-kl+c \qquad (12.2)$$

The value of constant of integration c can be determined using initial conditions. i.e. when l=0 then $I=I_o$. By applying initial conditions, we get

$$\ln I_o=-k(0)+c$$

$$\ln I_o=c \qquad (12.3)$$

By putting the value of c from equation 3 into equation 2, we get

$$\ln I=-kl+\ln I_o$$

$$\ln I-\ln I_o=-kl$$

$$\ln\left(\frac{I}{I_o}\right) = -kl$$

$$\ln\left(\frac{I_o}{I}\right) = kl \qquad (12.4)$$

The equation 12.4 is the equation of straight line passing through the origin. Plot of $\ln(I_o/I)$ vs l will be straight line with slope equal to k. The SI units of k can be evaluated from this expression as m^{-1}. Above expression can be rearranged in exponential form as

$$\ln\left(\frac{I}{I_o}\right) = -kl$$

$$\frac{I}{I_o} = e^{-kl}$$

$$I = I_o e^{-kl} \qquad (12.5)$$

It is clear from equation 12.5 that intensity of monochromatic beam of light decreases exponentially when thickness of the homogeneous medium increases arithmetically. Equation 12.4 can also be written as

$$2.303 \log\left(\frac{I}{I_o}\right) = -kl$$

$$\log\left(\frac{I}{I_o}\right) = -\frac{k}{2.303} l$$

$$\log\left(\frac{I}{I_o}\right) = -\varepsilon' l \qquad (12.6)$$

Where $\varepsilon' = k/2.303 = 0.4343$ k is called extinction coefficient. Its definition can be derived from equation 12.6 as "It is the reciprocal of the thickness of the medium which reduces the intensity of light to one tenth of the original value". i.e.

$$\log\left(\frac{\frac{I_o}{10}}{I_o}\right) = -\varepsilon' l$$

$$\log\left(\frac{I_o}{10} \times \frac{1}{I_o}\right) = -\varepsilon' l$$

$$\log\left(\frac{1}{10}\right) = -\varepsilon' l$$

$$-\log 10 = -\varepsilon' l$$

$$\log 10 = \varepsilon' l$$

$$1 = \varepsilon' l$$

$$\frac{1}{l} = \varepsilon'$$

So SI units of ε' are m^{-1} and its value depends upon the nature of the medium and wavelength of light used.

12.3.2 Beer's law

Lambert's law is applicable only to solids. Beer studied the effect of concentration of colored substance on absorption of light in 1852 and presented his results in the form of empirical law which is known as Beer's law. Beer's law can be stated as "the rate of decrease of intensity of light with respect to concentration of solution is directly proportional to intensity of light".

Mathematically Beer's law can be written as

$$-\frac{dI}{dC} \alpha I$$

Where I is the intensity of light at any concentration C and $-dI/dC$ is the rate of decrease of intensity of light with respect to concentration of absorbing colored substance in solution. By rearranging above expression, we get

$$-\frac{dI}{I} \alpha dC$$

$$-\frac{dI}{I} = k'dC$$

Where k' is proportionality constant and its value depends upon the wavelength used and nature of the absorbing substance. Its units are reciprocal of concentration units. The above equation can be integrated as

$$\int \frac{dI}{I} = -k' \int dC$$

$$\ln I = -k'C + \text{constant} \qquad (12.7)$$

The value of constant of integration can be evaluated using initial conditions i.e. when C=0 then I=Io. By applying initial conditions, we get

$$\ln I_o = -k'(0) + \text{constant}$$

$$\ln I_o = \text{constant} \qquad (12.8)$$

By putting the values of constant from equation 12.8 into equation 12.7, we get

$$\ln I = -k'C + \ln I_o$$

$$\ln I - \ln I_o = -k'C$$

$$\ln\left(\frac{I}{I_o}\right) = -k'C$$

Or

$$\ln\left(\frac{I_o}{I}\right) = k'C \qquad (12.9)$$

Equation 12.9 is the equation of straight line passing through the origin. The plot of $\ln(I_o/I)$ versus C will be a straight line with slope equal to k'. The units of k' can be evaluated from equation 12.9 which are M^{-1} when concentration is expressed in moldm^{-3}. Equation 12.9 can be rearranged in exponential form as

$$\ln\left(\frac{I}{I_o}\right) = -k'C$$

$$\frac{I}{I_o} = e^{-k'C} \qquad (12.10)$$

From equation 12.10, Beer's law can be stated as "The intensity of beam of monochromatic light passing through a solution decreases exponentially as the concentration of absorbing substance increases arithmetically".

Equation 12.9 can also be written as

$$2.303\log\left(\frac{I}{I_o}\right) = k'C$$

$$\log\left(\frac{I}{I_o}\right) = -\frac{k'}{2.303}C$$

$$\log\left(\frac{I}{I_o}\right) = -\varepsilon''C$$

Where $\varepsilon'' = \frac{k'}{2.303} = 0.4343\,k'$ is called extinction co-efficient and its units are dm^3 mol^{-1}.

12.3.3 Beer-Lambert's law

Beer's law and Lambert's law are usually combined and the combined law is known as Beer-Lambert's law. This law can be stated as "the rate of decrease of intensity of monochromatic beam of light with respect to thickness of the medium is directly proportional to the intensity of light and concentration of absorbing substance in solution".

Mathematically Beer-Lambert's law can be written as

$$-\frac{dI}{dl}\,\alpha I.C$$

Where I is the intensity of light, C is the concentration of absorbing substance in solution and –dI/dl is the rate of decrease of intensity of light with respect to thickness of medium or optical path length.

The above expression can be written as

$$-\frac{dI}{dl} = K.I.C \tag{12.11}$$

Where K is proportionality constant. Its value depends upon nature of absorbing material and wavelength of light used. Equation 12.11 is variable separable 1st order differential equation and it can be integrated by separating variables as

$$\int \frac{dI}{I} = -K.C\int dl$$

$$\ln I = -K.C.l + \text{constant} \tag{12.12}$$

The value of constant of integration can be determined using initial conditions i.e. when l=0 then I=Io. By applying these conditions on equation 12.12, we get

$$\ln I_o = \text{constant} \tag{12.13}$$

By putting the value of constant from equation 12.13 into equation 12.12, we get

$$\ln I = -K.C.l + \ln I_o$$

$$\ln\left(\frac{I}{I_o}\right) = -K.C.l$$

$$\ln\left(\frac{I_o}{I}\right) = K.C.l$$

$$2.303\log\left(\frac{I_o}{I}\right) = K.C.l$$

$$\log\left(\frac{I_o}{I}\right) = \frac{K}{2.303}.C.l$$

$$\log\left(\frac{I_o}{I}\right) = \varepsilon.C.l \tag{12.14}$$

Where ε is equal to K/2.303. It is called *molar extinction coefficient* or molar absorption coefficient or molar absorptivity when concentration is expressed in moldm^{-3} and optical path length in cm. Equation 12.14 can be rearranged in exponential form as

$$\log\left(\frac{I}{I_o}\right) = -\varepsilon.C.l$$

$$\frac{I}{I_o} = e^{-\varepsilon.C.l}$$

$$I = I_o e^{-\varepsilon.C.l}$$

The quantity '$\log(I_o/I)$' present in the left hand side of the equation 12.14 is called *absorbance*. Absorbance is a dimensionless quantity. It is denoted by A. The value of absorbance depends upon path length, concentration of absorbing substance and wavelength of light. Equation 12.14 is equation of straight line passing through the origin and it can be written as

$$A = \varepsilon.C.l \qquad (12.15)$$

The plot of A as function of C at particular wavelength (λ_{max}) and constant path length will be straight line with slope equal to εl. The value of ε can be determined from the slope of the plot. The definition of ε can be derived from equation 12.15 as

$$\varepsilon = \frac{A}{C.l}$$

If $C=1 moldm^{-3}$ and $l=1cm$ then

$$\varepsilon = A$$

Hence molar extinction coefficient (ε) can be defined as absorbance for a concentration of $1 moldm^{-3}$ and path length of 1cm. Equation 12.15 gives the absorbance of one substance as function of its concentration. According to Beer-Lambert's for multi-component system, the absorbance of mixture can be written as

$$A = A_1 + A_2 + A_3 + \ldots\ldots$$

$$A = \varepsilon_1.l.C_1 + \varepsilon_2.l.C_2 + \varepsilon_3.l.C_3 + \ldots\ldots$$

Where A is the total absorbance at particular wavelength, A_1, A_2 and A_3 are the values of absorbance of component 1, 2 and 3 respectively and ε_1, ε_2 and ε_3 are the values of molar extinction coefficients of components 1,2 and 3 respectively.

Another important quantity related to this law is transmittance. Transmittance is denoted by T. It can be defined as

$$T = \frac{I}{I_o} \qquad (12.16)$$

Where I_o is the intensity of incident light and I is the intensity of transmitted light. Transmittance is also a dimensionless quantity. The mathematical relation between absorbance and transmittance can be derived from definition of absorbance and transmittance as

$$A = \log\left(\frac{I_o}{I}\right) \qquad (12.17)$$

Equation 12.16 can be written as

$$\frac{1}{T} = \frac{I_o}{I} \qquad (12.18)$$

By putting the value of 1/T from equation 12.18 into equation 12.17, we get

$$A = \log\left(\frac{1}{T}\right)$$

$$A = -\log T \qquad (12.19)$$

Hence absorbance is equal to negative logarithm of transmittance. Both quantities are inter-convertible. If we have the value of one quantity, we can determine the other using equation 12.19.

12.3.4 Applications of Beer-Lambert's law

1. The value of molar extinction coefficient can be determined using Beer-Lambert's law by plotting absorbance as function of concentration at a particular path length.
2. By determination of ε and λ_{max}, we can identify the colored substance present in solution.
3. The unknown concentration of given colored solution can be determined from the plot of absorbance versus concentration using Beer-Lambert's law.

12.3.5 Limitations of Beer-Lambert's law

1. Beer-Lambert's law is only valid on monochromatic light.
2. This law is applicable under low concentration range where interactions between molecules are not taken into consideration.
3. This law is also invalid when radiations of very high intensities are used.

12.3.5 Deviations from Beer-Lambert's law

According to Beer-Lambert's law, the plot of absorbance as a function of concentration at a particular optical path length and wavelength of monochromatic beam of light should be a straight line passing through origin. At high concentrations, absorbance versus concentration plot deviates from linear behavior. The causes of deviation from Beer-Lambert's law are given below:

1. Presence of some external substances that absorbs or fluoresce at the wavelength of absorption can cause deviation from Beer-Lambert's law.
2. Deviations may occur when light of single wavelength is not used.
3. Polymerization of solutes during measurements may cause deviation.
4. Association, dissociation or ionization of solute may cause deviation from the law.
5. Improper slit width may cause deviation from the law.
6. Presence of impurities in colored compounds may also cause deviation from the law.

Example 12.1

A solution of a compound having concentration 0.214 mM placed in a cell of path length 1 cm transmits 25.5 % of light of a particular wavelength. Calculate the molar absorption coefficient of the solute.

Solution As we know that from given data

$$\%T = 25.5$$

Hence, $T = 0.255$

It is known that transmittance is the ratio of intensity of transmitted light to the intensity of incident light so,

$$\frac{I_t}{I_o} = 0.255$$

$$\frac{I_o}{I_t} = \frac{1}{0.255} \Rightarrow 3.921$$

$$\log\left(\frac{I_o}{I_t}\right) = 3.921$$

$$A = 0.593$$

As we know that

$$A = \varepsilon c l$$

By putting values in above equation we can get the value of absorption coefficient as follows

$$\varepsilon = \frac{0.593}{(1)(0.214 \times 10^{-3})}$$

$$\varepsilon = 2771.02\ \text{Lmol}^{-1}\text{cm}^{-1}$$

12.4 LAWS OF PHOTOCHEMISTRY

The basic laws of photochemistry are

1. Grothus-Drapper law
2. Stark-Einstein's law of photochemical equivalence

1. Grothus-Drapper law

This is known as 1st law of photochemistry **(also known as principle of photochemical activation)** and it can be stated as "*only absorbed light can cause a chemical reaction or only those radiations which are absorbed by a reacting system are effective in producing chemical change*". According to this law absorbed light may initiate reaction but it is not always true because absorbed light may re-emit in the form of fluorescence and phosphorescence. For a photochemical reaction it is necessary to absorb the light. So it is important to determine the intensity of light absorbed by a system. The intensity of absorbed light can be measured using definition of absorbance. According to this definition, absorbance in term of intensity of incident light and intensity of transmitted light is given by

$$A = \log\frac{I_o}{I_t}$$

Where, I_o is the intensity of incident light and I_t is the intensity of transmitted light. The quantity A is associated with concentration of solution (c) and path length (l) according to Beer-Lambert law which can be stated mathematically as

$$A = \varepsilon cl$$

Where, ε is called molar absorption coefficient. It is independent of concentration and path length. It is the characteristics of chromospheres.

By combining above equations, we get

$$\log\frac{I_o}{I_t} = \varepsilon cl$$

$$\frac{I_o}{I_t} = 10^{\varepsilon cl}$$

$$\frac{I_t}{I_o} = 10^{-\varepsilon cl}$$

$$I_t = I_o 10^{-\varepsilon cl} \qquad (12.20)$$

Intensity of incident light can be expressed as a sum of intensity of absorbed light and that of transmitted light i.e.

$$I_o = I_a + I_t \qquad (12.21)$$

$$I_a = I_o - I_t$$

By putting the value of I_t from equation (12.20) into equation (12.21), we get

$$I_a = I_o - I_o 10^{-\varepsilon cl}$$

$$I_a = I_o\left(1 - 10^{-\varepsilon cl}\right)$$

According to Grothus-Drapper law, only I_a is the cause of photochemical reaction. This law is purely qualitative and does not give any relationship between the amount of light absorbed by a system and the number of molecules which have reacted.

2. Stark-Einstein law's of photochemical equivalence

The quantitative aspects of photochemistry are explained by Johannes Stark and Albert Einstein in 1905 with the help of quantum theory of light by proposing a law. Stark-Einstein's law is 2nd law of photochemistry which is also named as photochemical equivalence law. It is stated as *"Any molecule or atom activated by light, absorbs only one quantum of light which causes the activation".* OR. *When a* *substance undergoes a photochemical change, each quantum of energy absorbed results in the decomposition of one molecule only.* They studied that each molecule taking part in the reaction absorbs only a single quantum or photon of light. The molecule that gains one photon-equivalent energy is activated and enters into reaction. This process is explained with the help of example as shown in Fig. 12.1. A molecule A absorbs one photon and becomes activated to carry out a photochemical reaction. Then activated molecule (A*) is converted into product (P).

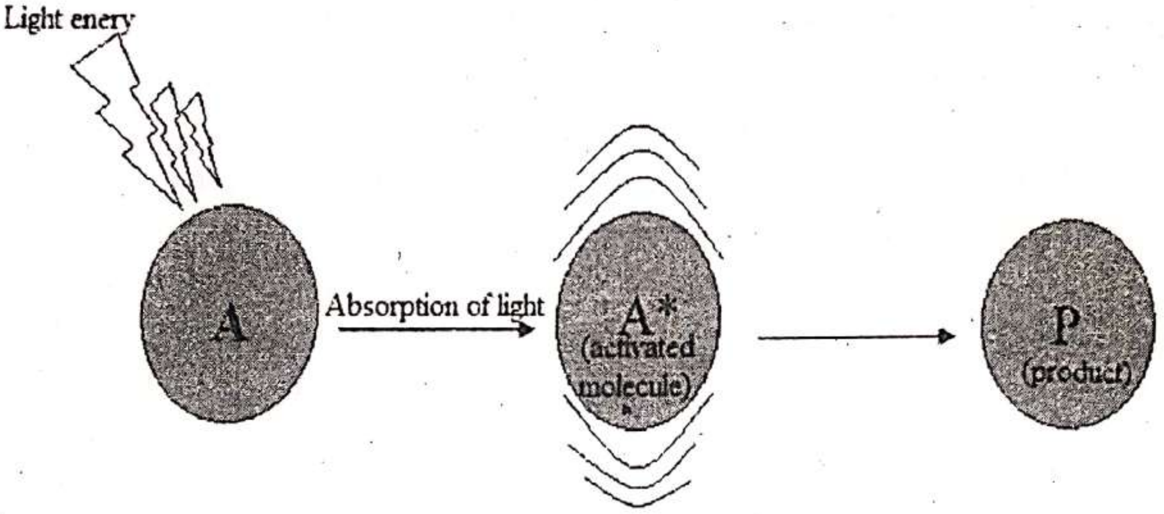


Fig. 12.1 Pictorial illustration of a photochemical reaction

When a photon is absorbed by a molecule, energy is transferred to a molecule. The amount of energy of a photon according to Planck's equation can be written as

$$E = \frac{hc}{\lambda} \tag{12.22}$$

Where, *h* is the Planck's constant (6.626×10^{-34} Js), c is the velocity of light in vacuum (3×10^{8} ms^{-1}), υ is the frequency of light absorbed and λ is the wavelength of light.

In chemistry reactants or products are given in term of moles instead of molecules. Therefore, photons are also expressed in terms of moles. One mole of photons is known as an *Einstein*. The amount of energy transferred to reactants by an Einstein is given by the equation

$$E = N_A \frac{hc}{\lambda} \tag{12.23}$$

From above relation it is inferred that energy is inversely proportional to wavelength of radiation absorbed. It means that higher the wavelength, the smaller will be the energy per Einstein. This law is concerned with the primary photochemical process in which one atom or molecule absorbs only one quantum of photon of light. Thus in the primary process, the number of molecules which are activated is equal to the number of quanta absorbed. An atom or molecule activated photochemically may initiate a sequence of reactions so that many reactant molecules may undergo chemical change through chain mechanism. In such cases, the number of reactant molecules transformed into product will be many times the number of photon absorbed. However, in some cases deactivation takes place and the number of reactant molecules suffering change will be less than the number of photon absorbed. Hence, Einstein law of photochemical equivalence should not be interpreted to mean that one atom or molecule will react per quantum of light absorbed, but that only one atom or molecule is activated by each quantum of radiation.

Example 12.2

Calculate the energy corresponding to the followings:

(i) $\bar{\upsilon} = 3650 \text{ cm}^{-1} = 3.65 \times 10^{5} \text{ m}^{-1}$

(ii) $\lambda = 1.544\, A^{o}$

(iii) $\upsilon = 5 \times 10^{15}\ Hz$

Solution

We know that

$$E = h\upsilon$$

And $$\upsilon = \frac{c}{\lambda}$$

Then, $$E = \frac{hc}{\lambda}$$

Where, $$\bar{\upsilon} = \frac{1}{\lambda}$$

So, above equation will be

$$E = hc\bar{\upsilon}$$

(i) $$E = hc\bar{\upsilon}$$

By putting values in above equation we get

$$E = 6.62 \times 10^{-34} \times 2.9979 \times 10^{8} \times 3.65 \times 10^{5}$$

$$E = 7.25 \times 10^{-20} \text{ J}$$

(ii) $$E = \frac{hc}{\lambda}$$

By putting values in above equation

$$E = \frac{6.62 \times 10^{-34} \times 2.9979 \times 10^{8}}{1.544 \times 10^{-10}}$$

$$E = 1.286 \times 10^{-15} \text{ J}$$

(iii) $E = h\upsilon$

By putting values in above equation we get

$$E = 6.62 \times 10^{-34} \times 5 \times 10^{15}$$

$$E = 3.313 \times 10^{-18} \text{ J}$$

12.5 QUANTUM YIELD AND ITS EXPERIMENTAL DETERMINATION

The law of photochemical equivalence applies to primary photochemical processes, i.e., where the products do not undergo further reaction. In such cases the number of molecules reacting will be equal to the number of energy quanta absorbed. What happens thereafter is beyond the scope of this law. In most cases, a molecule activated photochemically, may initiate a series of thermal reaction called secondary reactions. As a result of these secondary reactions many reactant molecules may undergo chemical changes by absorbing one quantum only. In such cases there will be no 1:1 ratio between reacting molecules and quanta of energy absorbed. In some cases, a molecule may be deactivated photochemically under deactivation. Then, less than one molecule may react per quantum of light radiation. To express the relationship between the number of molecules reacting with the number of photon absorbed, the concept of quantum yield or efficiency (ϕ) is introduced. Quantum yield measures the efficiency of a photochemical process and it indicates that whether the reaction is simple of complex.

"The number of molecules reacted per photon of light absorbed is known as quantum yield". It is expressed as

$$\phi = \frac{\text{No. of molecules undergoing the process}}{\text{No. of quanta absorbed}} \quad \text{or}$$

$$\phi = \frac{\text{No. of moles reacting in the given time}}{\text{No. of einsteins absorbed in the same time}}$$

It is observed that it is not necessary all photochemical reactions obey Einstein's law. The number of molecules undergoing the process in the presence of light is found to be different from the number of quanta absorbed in given time.

The quantum yield is equal to one for a photochemical reaction which obeys the photochemical equivalence law in which one molecule is converted into product per quanta. If more than one molecule are decomposed by absorbing one quantum the quantum yield of that reaction is greater than one. Similarly, the quantum yield is less than one for a photochemical reaction when number of decompose molecules is less than one per quanta. The quantum yield varies from 0 to 10^6. No matter how large or small ϕ may be, the law holds for primary photochemical process.

Reasons for high quantum yield

The following are the reasons for high quantum yield:

(i) Many photochemical reactions produce atoms or free radicals which initiate series of chain reactions in which more than one reactants undergo chemical change.

(ii) Formation of an intermediate product acting as a catalyst.

(iii) The reactions may be exothermic and as such the heat evolved may activate other molecules and thus react without absorption of other quanta of light.

(iv) The active molecule may collide with other molecules and activate them which in turn activate other molecules.

Reasons for low quantum yield

The various reasons are:

(i) Deactivation of excited molecules may takes place before they are able to form products.

(ii) Excited molecules may lose their energy by collision with non-excited molecules.

(iii) Molecules may not receive energy sufficient enough to enable them to react.

(iv) The primary photochemical process may be reversed.

(v) The dissociated fragments may recombine so as to give low yield.

Experimental method for determination of quantum yield of a photochemical reaction is given below.

A photochemical reaction takes place by the absorption of light by reacting molecules. Thus, it is necessary to determine the intensity of absorbed light to study the rate of photochemical reaction. For this purpose a reaction mixture is irradiated with light of a selected wavelength. A light source is used to emit the radiations of suitable intensity. Tungsten filament or mercury vapor lamps are used as a light source. The light beam coming from the source passes through the lens which is used to select the radiations of one wavelength. After passing through lens, light enters into monochromator or filter. Then, light enters into the sample cell having sample mixture which is kept in a thermostat. The sample cell used is made up of glass or quartz which is suitable for the entrance or exit of light. Glass cells are usually used when visible region radiations are required. But below 3500 Å only quartz cells are used. Finally, transmitted light from sample cell strikes the detector where its intensity is determined. Mostly used detectors for the measurement of intensity of transmitted light are thermopile, photoelectric cell and actinometer. A thermopile is essentially a multifunction thermocouple which is previously calibrated against a standard source of light. Instead, a commonly used actinometer is the uranyl oxalate actinometer consisting of 0.05 M oxalic acid and 0.01 M uranyl sulfate in water. On exposure to radiation the reaction takes place the extent of which can be ascertained by titrating the remaining oxalic acid with potassium permanganate. This reaction has a quantum yield of about 0.5.

$$UO_2^{2+} + h\nu \rightarrow (UO_2^{2+})^*$$

$$(UO_2^{2+})^* + H_2C_2O_4 \rightarrow CO_2\,(g) + CO\,(g) + H_2O\,(l)$$

Thus, the intensity of light is measured first with the empty cell and then the cell filled with sample mixture. In this way, first reading gives the intensity of incident light (I_o) and second reading gives the intensity of transmitted light (I) from sample mixture. The difference between these readings (I_o – I) gives the value of absorbed intensity by sample mixture. In this way it is possible to collect data on the rate of chemical reaction and light intensity, from which rate law and quantum yield can be determined. An experimental setup for determination of light intensity is shown in Fig. 12.2.

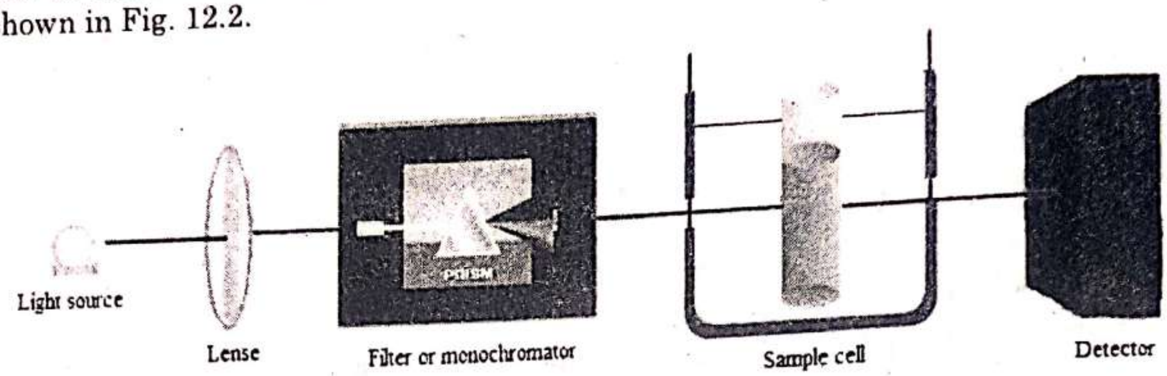


Fig. 12.2 Experimental setup for determination of absorbed intensity

12.6 PHOTOPHYSICAL PROCESSES

Light absorption by a system and relaxation of electronically excited species by various ways is called *photophysical process* because in such processes chemical change does not occur. Species absorb light and move into electronically excited states. This photophysical process is called *excitation*. System can lose this extra energy by different processes which are known as *relaxation processes*. These relaxation processes include radiative and non radiative relaxation processes. Internal conversion, intersystem crossing and vibrational relaxation are non radiative processes. Fluorescence and phosphorescence are radiative processes. All these photophysical processes can be explained on the basis of Jablonski diagrams as shown in Fig. 12.3. Alexander Jablonski, a Polish physicist who developed these diagrams to explain the kinetics of processes initiated by electronic transitions.

In Fig. 12.3, ground singlet state is shown by S_0 where, spin multiplicity is equal to one and electrons are in paired form. The first excited singlet state is shown by S_1 where spin multiplicity is equal to one. The first excited triplet state is shown by T_1 where, spin multiplicity is equal to three and electrons are not in paired form. Each electronic state (S_0, S_1 and T_1) has rotational and vibrational energy levels. But for simplicity only vibrational levels are shown in Fig. 12.3. The lowest vibrational level of each electronic state is shown by dark horizontal lines and higher vibrational levels are shown by lighter horizontal lines. The radiative and non radiative processes are shown by solid and wavy arrows respectively. The loss of excess electronic energy through emission of photon is called a radiative process and the loss of excess electronic energy without emission of photon is called non radiative relaxation process. We shall briefly describe these photophysical processes on the basis of Jablonski diagrams given in Fig. 12.3.

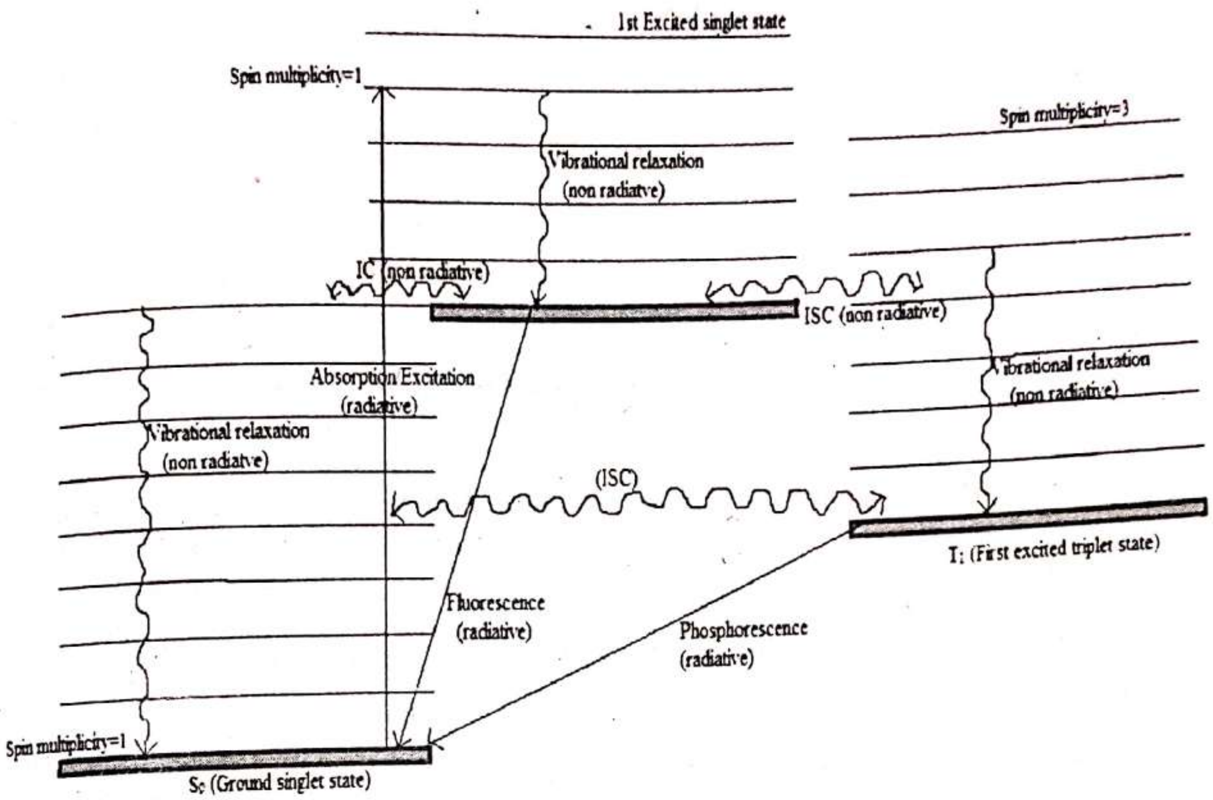


Fig. 12.3 Jablonski diagram indicating radiative (solid arrows) and non radiative (wavy arrows) processes.

12.7 NON RADIATIVE RELAXATION PROCESSES

Vibrational relaxation (VR), internal conversion (IC) and intersystem crossing (ISC) are non radiative processes. The transition from higher vibrational level to lower vibrational level of an electronic state (S_0, S_1 or T_1) without emission of light is called *vibrational relaxation*. The decay from the lowest vibrational level of S_1 to a high vibrational level of S_0 is referred to as *internal conversion*. Internal conversion schematically can be represented as $S_1 \rightarrow S_0$ and its rate will be equal to $k_{ic}[S_1]$ where, k_{ic} is the rate constant for internal conversion and $[S_1]$ is the concentration of species in first excited electronic state at any time t.

Intersystem crossing involves spin change. The transition from S_1 to T_1 or T_1 to S_0 is referred to as *intersystem crossing*. The rate of process $S_1 \xrightarrow{k_{isc}^s} T_1$ will be equal to $k_{isc}^s[S_1]$ where, k_{isc}^s is the 1st order rate constant for intersystem crossing for S_1 to T_1 transition. Similarly the rate of the process $T_1 \xrightarrow{k_{isc}^T} S_0$ will be to $k_{isc}^T[S_1]$ where k_{isc}^T is the 1st order rate constant for intersystem crossing for T_1 to S_0 transition.

12.8 RADIATIVE RELAXATION PROCESSES

Fluorescence and phosphorescence are radiative relaxation processes. Fluorescence is the emission of radiation that causes molecular transition from an excited to a ground state without change in spin multiplicity. Since electrons in molecules are paired according to the Pauli exclusion principle, the initial absorption is from the ground-state singlet S_0 to the first excited singlet S_1(or some higher singlet level). At first glance, fluorescence might appear to exactly reverse of the absorption process. This is true on the atomic level, but comparing the absorption and emission spectra of molecules shows them not to be superimposed on each other. Instead, they form the mirror image of each other, with the emission spectrum displaced toward the longer wavelength (Figure12.3). Since the time required to execute a vibration (about 10^{-14} to 10^{-13} s) is much faster than the decay or mean lifetime (about 10^{-9} to 10^{-9} s) of the fluorescent state, most of the excess vibrational energy dissipates to the surroundings as heat, and the excited molecules now decay from their ground vibrational levels. While phosphorescence offers a different path for the return of an excited molecule to the ground state with the emission of light. Phosphorescence can be readily distinguished from fluorescence by two characteristics. First, phosphorescence has a much longer decay period than fluorescence, about 10^{-3} s to several seconds. Second, a molecule in the phosphorescent state is paramagnetic containing two unpaired electrons; that is, it is a triplet state (Figure 12.3). Initially, an electron is promoted from S_o to S_1. The promotion is followed by a process called radiationless transition, in which the electron flips its spin and drops from S_1 to T_1, the lowest triplet level, without emission of light. In the end, a radiative transition from T_1 to S_o occurs. This step is called Phosphorescence.

Fluorescence is a radiative relaxation process in which photons are emitted as a result of transition from S_1 to S_o without change in spin multiplicity. So the process of fluorescence can be represented schematically in the following way

$$S_1 \xrightarrow{k_f} S_0 + h\nu$$

The rate of fluorescence process can be written as

$$\upsilon_f = k_f[S_1] \tag{12.24}$$

Where υ_f is the rate of fluorescence, k_f is the 1st order rate constant for fluorescence and $[S_1]$ is the concentration of fluorescent material at electronically excited state S_1 at any time t. the units of k_f are s^{-1}.

Another radiative process is phosphorescence. It is relaxation process in which photons are emitted as a result of transition from first excited triplet state (T_1) to the ground state (S_o) with change in spin multiplicity. The process of phosphorescence is slow as compared to that of fluorescence. Phosphorescence schematically can be written as

$$T_1 \xrightarrow{k_p} S_0 + h\nu$$

The rate of phosphorescence is

$$\upsilon_p = k_p[T_1] \tag{12.25}$$

Where υ_p is the rate of phosphorescence, k_p is the 1st order rate constant for phosphorescence and $[T_1]$ is the concentration of species in first excited triplet state T_1. The units of k_p are s^{-1}.

12.9 QUANTITATIVE ASPECTS OF FLUORESCENCE

For kinetic description of photophysical processes, Jablonski diagram can be modified to simplify the processes as shown in Fig. 12.4. The process of absorption, fluorescence, internal conversion, intersystem crossing and phosphorescence along with their respective rate constants are shown in Fig. 12.4.

Fig. 12.4 can be used to develop various expressions in the presence and absence of quencher.

12.9.1 Fluorescence life time in the absence of quencher

The rate of consumption of species in first excited singlet state (S_1) as a result of relaxation processes can be written as

$$d[S_1]/dt = -K_f[S_1] - K_{ic}[S_1] - K^S_{isc}[S_1]$$

$$d[S_1]/dt = -(K_f + K_{ic} + K^s_{isc})[S_1]$$

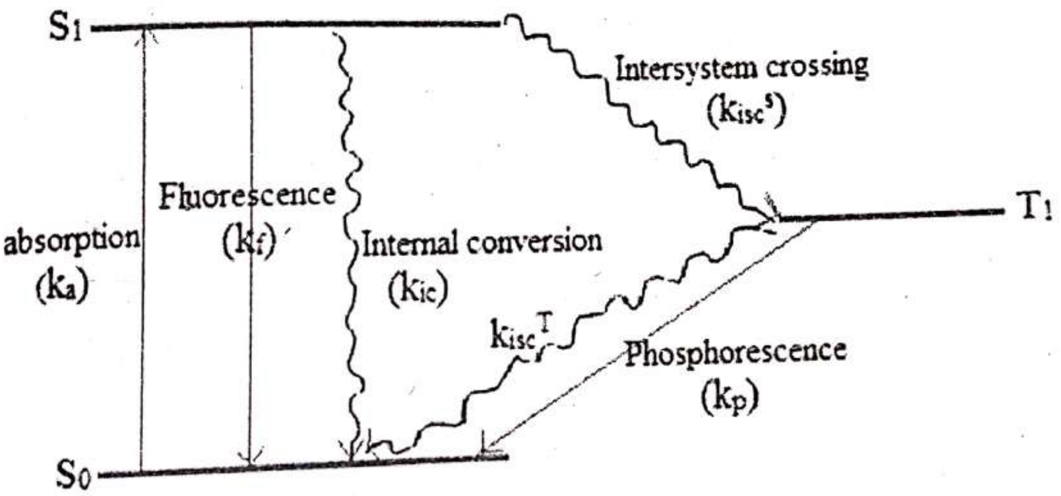


Fig. 12.4 kinetic description of photophysical processes i.e. radiative (solid arrows) and non radiative (wavy arrows)

By separating variables and integrating above equation, we get

$$\int d[S_1]/[S1] = -(K_f + K_{ic} + K^s_{isc})\int dt$$

$$\ln[S_1] = -(K_f + K_{ic} + K^s_{isc})t + c \qquad (12.26)$$

The value of constant of integration c can be obtained using initial conditions. i.e when $t = 0$, then $[S_1] = [S_1]_0$ by putting these values in equation (12.26), we get

$$\ln[S_1]_0 = c$$

By putting value of c in equation (12.26), we get

$$\ln[S_1] = -(K_f + K_{ic} + K^s_{isc})t + \ln[S_1]_0$$

$$\ln[S_1]-\ln[S_1]_0=-(K_f+K_{ic}+K^s_{isc})t$$

$$\ln[S_1]/[S_1]_0=-(K_f+K_{ic}+K^s_{isc})t$$

$$[S_1]/[S_1]_0=e^{-(K_f+K_{ic}+K^s_{isc})t}$$

$$[S_1]=[S_1]_0e^{-(K_f+K_{ic}+K^s_{isc})t} \qquad (12.2)$$

According to this expression, the value of concentration of species at first excited electronic state (S_1), decreases exponentially with time due to relaxation processes as shown in Fig. 12.5.

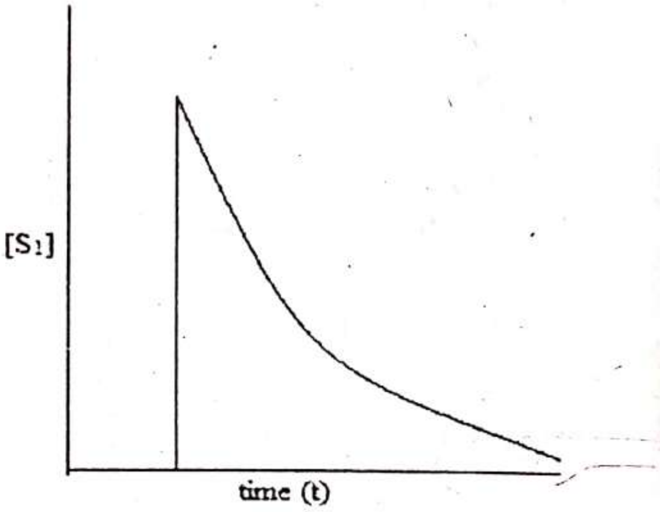


Fig. 12.5 Variation of concentration of specie at first excited singlet state with time

The fluorescence life time can be defined as *"the time for which [S₁] becomes 1/e times of initial concentration".* Therefore

$$t=\tau_f^o$$

When $[S_1]=\frac{[S_1]_o}{e}$ then so equation 12.27 will be

$$[S_1]_o/e=[S_1]_0e^{-(K_f+K_{ic}+K^s_{isc})t}$$

$$e^{-1}=e^{-(K_f+K_{ic}+K^s_{isc})\tau^0_f}$$

$$-1=-(K_f+K_{ic}+K^s_{isc})\tau^o_f$$

$$1=(K_f+K_{ic}+K^s_{isc})\tau^o_f$$

$$\tau_f^0=\frac{1}{\left(k_f+k_{ic}+k^s_{isc}\right)} \qquad (12.28)$$

This is the expression for fluorescence life time in terms of rate constants for fluorescence, internal conversion and intersystem crossing. Fluorescence life time decreases with increase of values of these rate constants.

12.9.2 Fluorescence quantum yield without quencher

The fluorescence quantum yield can be defined as ratio of rate constant for fluorescence to the sum of rate constants of all relaxation processes.

Mathematically, it can be written as

$$\phi_f^0=\frac{k_f}{k_f+k_{ic}+k^s_{isc}} \qquad (12.29)$$

So, fluorescence quantum yield depends upon the value of rate constants associated with fluorescence, internal conversion and intersystem crossing. It increases with increase of k_f and decreases with increase of k_{ic} and k^s_{isc}. It becomes maximum when sum of k_{ic} and k^s_{isc} is negligible as compared to k_f. Fluorescence quantum yield can also be defined as number of photons emitted as a result of fluorescence divided by total number of photons absorbed.

12.9.3 Fluorescence life time in the presence of quencher

The decrease in the rate of fluorescence in the presence of an external substance due to the collision of electronically excited molecules with molecules of external substance is called *fluorescence quenching*. The foreign substance is called *quencher*. Quencher removes excess electronic energy from molecules and converts it from state S_1 to S_0 as shown below.

$$S_1 + Q \xrightarrow{Kq} S_0 + Q$$

The rate expression for non radiative quenching process can be written as

$$v_q = k_q[S_1][Q]$$

Where, v_q is rate of quenching, k_q is bimolecular, second order rate constant for quenching process. [Q] is the available concentration of quencher and $[S_1]$ is the concentration of species in first excited electronic state. The rate of decrease of concentration of species at first excited electronic state as a result of internal conversion, intersystem crossing, fluorescence and quenching process can be written as

$$d[S_1]/dt = -K_f[S_1] - K_{ic}[S_1] - K^s_{isc}[S_1] - Kq[S_1][Q]$$

$$d[S_1]/dt = -\{K_f + K_{ic} + K^s_{isc} + K_q[Q]\}[S_1]$$

By separating variables and integrating above equation

$$\int d[S_1]/[S_1] = -\{K_f + K_{ic} + K^s_{isc} + K_q[Q]\}\int dt$$

$$\ln[S_1] = -\{K_f + K_{ic} + K^s_{isc} + K_q[Q]\}t + c \qquad (12.30)$$

We can determine the value of constant (c) by applying boundary conditions

When $t = 0$ then $[S_1] = [S_1]_0$ so, equation (12.30) will be

$$\ln[S_1]_0 = c$$

By putting this value of c in equation (12.30), we get

$$\ln[S_1] = -\{K_f + K_{ic} + K^s_{isc} + K_q[Q]\}t + \ln[S_1]_0$$

$$\ln[S_1] - \ln[S_1]_0 = -\{K_f + K_{ic} + K^s_{isc} + K_q[Q]\}t$$

$$\ln[S_1]/[S_1]_0 = -\{K_f + K_{ic} + K^s_{isc} + K_q[Q]\}t$$

$$[S_1]/[S_1]_0 = e - \{K_f + K_{ic} + K^s_{isc} + K_q[Q]\}t$$

$$[S_1] = [S_1]_0 e - \{K_f + K_{ic} + K^s_{isc} + K_q[Q]\}t \qquad (12.31)$$

Hence, population at S₁ exponentially decreases with time more rapidly in the presence of quencher as compared to that in the absence of quencher.

Fluorescence life time expression can be derived using condition:

When, $[S_1] = \frac{[S_1]_0}{e}$ then $t = \tau_f$ So, equation (12.31) will be

$$[S_1]_0 / e = [S_1]_0 e^{-\{K_f + K_{ic} + K^s_{isc} + K_q[Q]\}\tau_f}$$

$$e^{-1} = e^{-\{K_f + K_{ic} + K^s_{isc} + K_q[Q]\}\tau_f}$$

$$1 = \{K_f + K_{ic} + K^s_{isc} + K_q[Q]\}\tau_f$$

Hence, fluorescence life time in the presence of quencher can be written as

$$\tau_f = \frac{1}{\{k_f + k_{ic} + k^s_{isc} + k_q[Q]\}} \qquad (12.32)$$

So, value of fluorescence life time decreases with increase of quencher concentration.

12.9.4 Fluorescence quantum yield with quencher

According to definition of fluorescence quantum yield, the expression for it in the presence of quencher can be written as

$$\phi_f = \frac{k_f}{k_f + k_{ic} + k^s_{isc} + k_q[Q]} \qquad (12.33)$$

Hence, fluorescence quantum yield decreases by addition of quencher. The value of ϕ_f decreases with increase of concentration of quencher.

Example 12.3

Calculate the value of fluorescence quantum yield for $\tau_f = 1 \times 10^{-10}$ s and $k_{ic} = 5 \times 10^8 s^{-1}$ by assuming that rate constants for intersystem crossing and fluorescence quenching are small.

Solution

As we know that

$$\phi_f = \frac{k_f}{k_f + k_{ic} + k_{isc} + k_q[Q]}$$

Since, k_{isc} and $k_q[Q]$ are negligible. So, above equation will be

$$\phi_f = \frac{k_f}{k_f + k_{ic}} \qquad \text{(i)}$$

$$\tau_f = \frac{1}{k_f + k_{ic}}$$

$$1\times10^{-10} = \frac{1}{k_f + k_{ic}}$$

$$k_f + k_{ic} = \frac{1}{1\times10^{-10}}$$

$$k_f + k_{ic} = 1\times10^{10} \qquad \text{(ii)}$$

By putting value of k_{ic} from given data in above equation we get

$$k_f + 5\times10^{8} = 1\times10^{10}$$

$$k_f = 1\times10^{10} - 5\times10^{8}$$

$$k_f = 9.5\times10^{9}\ s^{-1} \qquad \text{(iii)}$$

By putting values of $k_f + k_{ic}$ and k_f from equation (ii) and (iii) respectively into equation (i) we get the value of ϕ_f.

$$\phi_f = 9.5\times10^{9} \times 1\times10^{-10}$$

$$\phi_f = 0.95$$

Example 12.4

If $k_{ic} = 1\times10^{7}s^{-1}$, $k_f = 2\times10^{7}s^{-1}$ and $k^{s}_{isc} = 1\times10^{8}s^{-1}$ calculate the fluorescence life time and fluorescence quantum yield in the absence of quencher.

Solution

As we know that

$$\tau_f^o = \frac{1}{\left(k_f + k_{ic} + k^{s}_{isc}\right)}$$

By putting values from data in above equation we get

$$\tau_f^o = \frac{1}{\left(2\times10^{7}\right) + \left(1\times10^{7}\right) + \left(1\times10^{8}\right)}$$

$$\tau_f^o = 7.69\times10^{-9}s$$

$$\tau_f^o = 7.69 \text{ ns}$$

The formula of fluorescence quantum yield is given as

$$\phi_f^o = \frac{k_f}{k_f + k_{ic} + k_{isc}^s}$$

By putting values from data we can get

$$\phi_f^o = \frac{2\times10^7}{\left(2\times10^7\right)+\left(1\times10^7\right)+\left(1\times10^8\right)}$$

$$\phi_f^o = 0.1538$$

12.9.5 Stern-Volmer equation in terms of fluorescence life time

A mathematical expression between fluorescence life time and quencher concentration can be presented which is known as Stern-Volmer equation.

Dividing equation (12.28) by (12.32), we get

$$\tau_f{}^0 / \tau_f = 1 / K_f + K_{ic} + K^s{}_{isc} \times K_f + K_{ic} + K^s{}_{isc} + K_q[Q] / 1$$

$$\tau_f{}^0 / \tau_f = K_f + K_{ic} + K^s{}_{isc} / K_f + K_{ic} + K^s{}_{isc} \times K_q[Q] / K_f + K_{ic} + K^s{}_{isc}$$

$$\tau_f{}^0 / \tau_f = 1 + K_q\tau^0{}_f[Q]$$

$\frac{\tau_f^0}{\tau_f}$ versus [Q] is a straight line equation with intercept form where intercept is equal to unity and slope of the plot is equal to $k_d\tau_f^0$. The value of k_d can be determined from the slope. This expression is called Stern-Volmer equation.

When $k_f >>>>> k_{ic} + k_{isc}^s$ then

$$\tau_f = \frac{1}{k_f + k_q[Q]}$$

$$1/\tau_f = K_f + K_q[Q]$$

This is an equation of straight line as shown in Fig. 12.6.

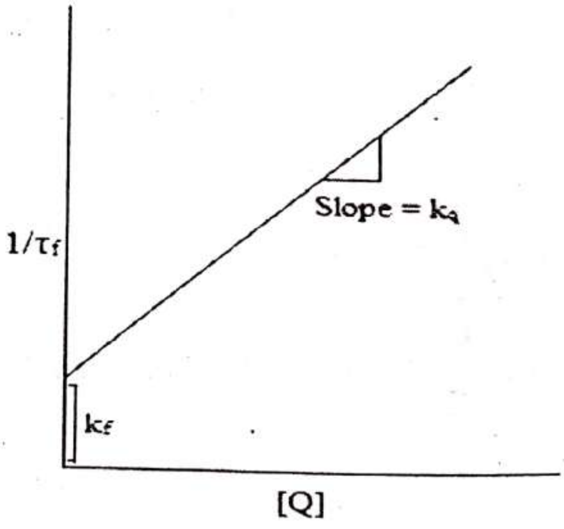


Fig. 12.6 Plot of $1/\tau_f$ versus [Q]

1. Stern-volmer equation in terms of fluorescence quantum yield

Dividing equation (12.29) by (12.33), we get

$$\phi^0{}_f / \phi_f = K_f / K_f + K_{ic} + K^s{}_{isc} \times K_f + K_{ic} + K^s{}_{isc} + K_q[Q] / K_f$$

$$\phi^0{}_f / \phi_f = 1 + K_q\tau^0{}_f[Q]$$

$\frac{\phi_f^0}{\phi_f}$ versus [Q] is an equation of straight line with y intercept $\phi^0_f / \phi_f = 1 + K_q \tau^0_f [Q]$ which is equal to one and slope is equal to $k_q \tau_f^0$.

2. Stern-Volmer equation in the form of fluorescence intensity

The net rate of formation of species at first excited electronic state S_1 as a result of absorption and relaxation in the presence of quencher can be written as

$$\frac{d[S_1]}{dt} = k_a[S_o] - k_f[S_1] - k_{ic}[S_1] - k^s_{isc}[S_1] - k_q[S_1][Q]$$

Using steady state approximation, we get

$$0 = k_a[S_o] - k_f[S_1] - k_{ic}[S_1] - k^s_{isc}[S_1] - k_q[S_1][Q]$$

$$k_a[S_o] = k_f[S_1] + k_{ic}[S_1] + k^s_{isc}[S_1] + k_q[S_1][Q]$$

$$k_a[S_o] = \{k_f + k_{ic} + k^s_{isc} + k_q[Q]\}[S_1]$$

Using equation (12.32), we get

$$\frac{[S_1]}{\tau_f} = k_a[S_o]$$

$$[S_1] = k_a[S_o]\tau_f \tag{12.34}$$

The fluorescence intensity is the rate of fluorescence which can be written as

$$I_f = k_f[S_1]$$

By putting value of $[S_1]$ from equation (12.34) into above equation we get

$$I_f = k_f k_a \tau_f [S_o] \tag{12.35}$$

Equation (12.35) is expression for fluorescence intensity in the presence of quencher in terms of rate constants for fluorescence and absorption process, fluorescence life time and concentration of fluorescent material in ground singlet state. The same expression in the absence of quencher can be written as

$$I_f^o = k_f k_a \tau_f^o [S_o] \tag{12.36}$$

Dividing equation (12.36) by equation (12.35), we get

$$\frac{I_f^o}{I_f} = \frac{k_f k_a \tau_f^o [S_o]}{k_f k_a \tau_f [S_o]}$$

$$\frac{I_f^o}{I_f} = \frac{\tau_f^o}{\tau_f} \tag{12.37}$$

By putting values of τ_f^o and τ_f from equation (12.28) and (12.32) respectively into equation (12.37), we get

$$\frac{I_f^o}{I_f} = \frac{1}{k_f + k_{ic} + k_{isc}^s} \cdot \frac{k_f + k_{ic} + k_{isc}^s + k_q[Q]}{1}$$

$$\frac{I_f^o}{I_f} = \frac{k_f + k_{ic} + k_{isc}^s}{k_f + k_{ic} + k_{isc}^s} + \frac{k_q}{k_f + k_{ic} + k_{isc}^s}[Q]$$

$$\frac{I_f^o}{I_f} = 1 + \frac{k_q}{k_f + k_{ic} + k_{isc}^s}[Q] \qquad (12.38)$$

Using equation (12.28), we get

$$\frac{I_f^o}{I_f} = 1 + k_q \tau_f^o [Q] \qquad (12.39)$$

Equation (12.39) is an equation of straight line in intercept form and can be used for determination of k_q by plotting $\frac{I_f^o}{I_f}$ as a function of quencher concentration as shown in Fig. 12.7.

When $k_f >>> k_{ic} + k_{isc}$ then equation (12.38) can be written as

$$\frac{I_f^o}{I_f} = 1 + \frac{k_q}{k_f}[Q]$$

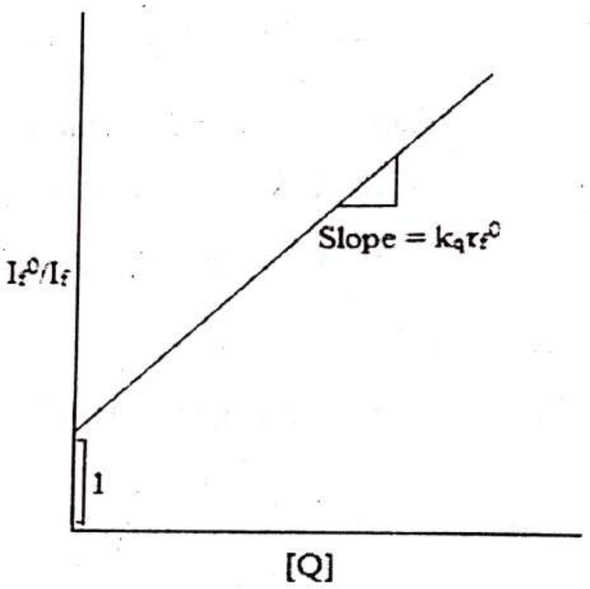


Fig. 12.7 Plot of I_f^0/I_f as a function of quencher concentration [Q]

According to this expression $\frac{I_f^o}{I_f}$ as a linear function of concentration of quencher with intercept equal to one and slope equal to $\frac{k_q}{k_f}$.

Example 12.5

The Stern-volmer equation for fluorescence quenching is

$$\frac{\phi_f^o}{\phi_f} = 1 + \frac{k_q}{k_f + k_{ic} + k_{isc}^s}[Q]$$

Where, $\frac{k_q}{k_f + k_{ic} + k_{isc}^s}$ is called quenching constant and is denoted by k_{sv}.

Calculate the value of k_{sv} for the data

$$k_f = 2\times10^{-5}\ s^{-1},\ k_{ic} = 3\times10^{-4}\ s^{-1},\ k_{isc}^s = 4\times10^{-2}\ s^{-1},\ k_q = 4.10\times10^{11}\ dm^3 mol^{-1} s^{-1}$$

Solution

$$k_{sv} = \frac{k_q}{k_f + k_{ic} + k_{isc}^s}$$

By putting values in above equation we get

$$k_{sv} = \frac{4.10\times10^{11}}{\left(2\times10^{-5}\right)+\left(3\times10^{-4}\right)+\left(4\times10^{-2}\right)}$$

$$k_{sv} = 1.7\ Lmol^{-1}$$

12.10 KINETIC ASPECTS OF PHOSPHORESCENCE

The process of phosphorescence includes the radiative transitions from triplet state to ground singlet state which is the lowest vibrational level as shown in Fig. 12.8.

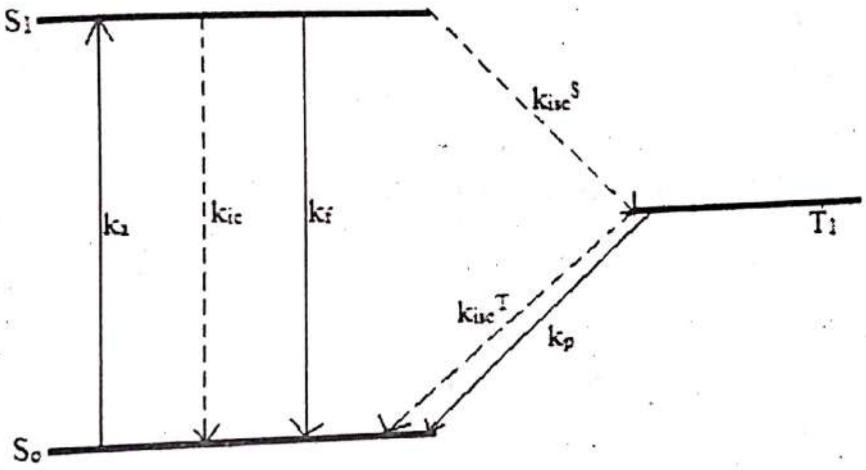


Fig. 12.8 Kinetic illustration of photophysical processes

Scheme of this process is

$$T_1 \xrightarrow{k_p} S_0 + h\upsilon$$

Rate of above reaction can be written as

$$\upsilon_p = k_p[T_1]$$

Where v_p is the rate of phosphorescence, k_p is the phosphorescence first rate constant having units s^{-1}.

Delay rate of $[T_1]$ is

$$\frac{d[T_1]}{dt} = -k_p[T_1] - k_{isc}^T[T_1]$$

$$\frac{d[T_1]}{dt} = -\left(k_p + k_{isc}^T\right)[T_1]$$

By separating variables and integrating above equation we get

$$\int \frac{d[T_1]}{[T_1]} = -\left(k_p + k_{isc}^T\right)\int dt$$

$$\ln[T_1] = -\left(k_p + k_{isc}^T\right)t + c \qquad (12.40)$$

When t = 0 then $[T_1] = [T_1]_o$ so, equation (12.40) will be

$$\ln[T_1]_o = c$$

By putting value of c in equation (12.40), we get

$$\ln[T_1] = -\left(k_p + k_{isc}^T\right)t + \ln[T_1]_o$$

$$\ln[T_1] - \ln[T_1]_o = -\left(k_p + k_{isc}^T\right)t$$

$$\ln\frac{[T_1]}{[T_1]_o} = -\left(k_p + k_{isc}^T\right)t$$

$$\ln\frac{[T_1]_o}{[T_1]} = \left(k_p + k_{isc}^T\right)t \qquad (12.41)$$

This is an equation of straight line passing through the origin. This equation can be used for the determination of sum of k_p and k_{isc}^T because the slope of the plot of $\ln\frac{[T_1]_o}{[T_1]}$ versus time is equal to $k_p + k_{isc}^T$.

12.10.1 Relation of Phosphorescence Life Time

$$\ln\frac{[T_1]}{[T_1]_o} = -\left(k_p + k_{isc}^T\right)t$$

$$\frac{[T_1]}{[T_1]_o} = e^{-\left(k_p + k_{isc}^T\right)t}$$

$$[T_1] = [T_1]_o e^{-\left(k_p + k_{isc}^T\right)t}$$

When $[T_1] = \frac{[T_1]_o}{e}$, then $t = \tau_p^o$. So

$$\frac{[T_1]_o}{e} = [T_1]_o e^{-\left(k_p + k_{isc}^T\right)\tau_p^o}$$

$$e^{-1} = e^{-\left(k_p + k_{isc}^T\right)\tau_p^o}$$

$$1 = \left(k_p + k_{isc}^T\right)\tau_p^o$$

$$\tau_p^o = \frac{1}{\left(k_p + k_{isc}^T\right)} \tag{12.42}$$

This is the phosphorescence life time in the absence of quencher.

12.11.2 Quantum Yield of Phosphorescence

$$\phi_p^o = \frac{\text{Rate of phosphorescence emission}}{\text{Rate of absorption of radiation}}$$

$$\phi_p^o = \frac{k_p[T_1]}{I_a} \tag{12.43}$$

Net rate of formation of $[S_1]$ is

$$\frac{d[S_1]}{dt} = I_a - k_{ic}[S_1] - k_f[S_1] - k_{isc}^s[S_1]$$

By applying steady state approximation, we get

$$0 = I_a - k_{ic}[S_1] - k_f[S_1] - k_{isc}^s[S_1]$$

$$I_a = \left(k_f + k_{ic} + k_{isc}^s\right)[S_1]$$

$$[S_1] = \frac{I_a}{k_f + k_{ic} + k_{isc}^s} \tag{12.44}$$

Similarly, net rate of formation of $[T_1]$ is

$$\frac{d[T_1]}{dt} = k_{isc}^s[S_1] - k_{isc}^T[T_1] - k_p[T_1]$$

By applying steady state approximation, we get

$$0 = k_{isc}^s[S_1] - k_{isc}^T[T_1] - k_p[T_1]$$

$$\left(k_p + k_{isc}^T\right)[T_1] = k_{isc}^s[S_1]$$

$$\left(k_p + k_{isc}^T\right)[T_1] = k_{isc}^s[S_1]$$

$$[T_1] = \frac{k_{isc}^s[S_1]}{\left(k_p + k_{isc}^T\right)} \tag{12.45}$$

By substituting value of $[S_1]$ from equation (12.44) into equation (12.45), we get

$$[T_1] = \frac{k_{isc}^s}{k_p + k_{isc}^T} \cdot \frac{I_a}{k_f + k_{ic} + k_{isc}^s}$$

$$[T_1] = \frac{I_a k_{isc}^s}{\left(k_p + k_{isc}^T\right)\left(k_f + k_{ic} + k_{isc}^s\right)}$$

By putting the value of $[T_1]$ in equation (12.43), we get

$$\phi_p^{o} = \frac{k_p k_{isc}^{s}}{\left(k_p + k_{isc}^{T}\right)\left(k_f + k_{ic} + k_{isc}^{s}\right)} \tag{12.46}$$

12.10.3 Phosphorescence Quenching

Deactivation by another molecule called quencher and the process is called quenching. Quenching provides a way for determination of rate constant of phosphorescence and rate constant for quenching.

12.10.4 Phosphorescence Life Time in the Presence of Quencher

$$T_1 + Q \xrightarrow{k_q} S_o + Q$$

Delay rate of $[T_1]$ is

$$\frac{d[T_1]}{dt} = -k_p[T_1] - k_{isc}^{T}[T_1] - k_q[Q][T_1]$$

$$\frac{d[T_1]}{dt} = -\left\{k_p + k_{isc}^{T} + k_q[Q]\right\}[T_1]$$

By separating variables and integrating above equation, we get

$$\int \frac{d[T_1]}{[T_1]} = -\left\{k_p + k_{isc}^{T} + k_q[Q]\right\}\int dt$$

$$\ln[T_1] = -\left\{k_p + k_{isc}^{T} + k_q[Q]\right\}t + c \tag{12.47}$$

When $t = 0$, then $[T_1] = [T_1]_o$ so, equation (12.47) will be

$$\ln[T_1]_o = c$$

By putting value of c in equation (12.47), we get

$$\ln[T_1] = -\left\{k_p + k_{isc}^{T} + k_q[Q]\right\}t + \ln[T_1]_o$$

$$\ln[T_1] - \ln[T_1]_o = -\left\{k_p + k_{isc}^{T} + k_q[Q]\right\}t$$

$$\ln\frac{[T_1]}{[T_1]_o} = -\left\{k_p + k_{isc}^{T} + k_q[Q]\right\}t$$

$$\ln\frac{[T_1]_o}{[T_1]} = \left\{k_p + k_{isc}^{T} + k_q[Q]\right\}t$$

This is an equation of straight line passing through origin with slope equal to $k_p + k_{isc}^{T} + k_q[Q]$.

$$\frac{[T_1]}{[T_1]_o} = e^{-\left\{k_p + k_{isc}^{T} + k_q[Q]\right\}t}$$

$$[T_1] = [T_1]_0 e^{-\{k_p + k_{isc}^T + k_q[Q]\}t} \qquad (12.48)$$

When $[T_1] = \frac{[T_1]_0}{e}$ then $t = \tau_p$ so, equation (12.48) will be

$$\frac{[T_1]_0}{e} = [T_1]_0 e^{-\{k_p + k_{isc}^T + k_q[Q]\}\tau_p}$$

$$e^{-1} = e^{-\{k_p + k_{isc}^T + k_q[Q]\}\tau_p}$$

$$1 = \{k_p + k_{isc}^T + k_q[Q]\}\tau_p$$

$$\tau_p = \frac{1}{k_p + k_{isc}^T + k_q[Q]} \qquad (12.49)$$

This is the phosphorescence life time in the presence of quencher. With the increase of quencher concentration, phosphorescence time decreases.

12.10.5 Quantum Yield of Phosphorescence in the Presence of Quencher

$$\phi_p = \frac{\text{Rate of phosphorescence emission in the presence of quencher}}{\text{Rate of absorption}}$$

$$\phi_p = \frac{k_p[T_1]}{I_a} \qquad (12.50)$$

Net rate of formation of $[S_1]$

$$\frac{d[S_1]}{dt} = I_a - k_{ic}[S_1] - k_f[S_1] - k_{isc}^s[S_1]$$

By applying steady state approximation

$$0 = I_a - k_{ic}[S_1] - k_f[S_1] - k_{isc}^s[S_1] \perp$$

$$I_a = \{k_{ic} + k_f + k_{isc}^s\}[S_1]$$

$$[S_1] = \frac{I_a}{k_{ic} + k_f + k_{isc}^s} \qquad (12.51)$$

Similarly, the net rate of formation of $[T_1]$ in the presence of quencher is

$$\frac{d[T_1]}{dt} = k_{isc}^S[S_1] - k_p[T_1] - k_{isc}^T[T_1] - k_q[Q][T_1]$$

By applying steady state approximation, we get

$$k_{isc}^S[S_1] = \{k_p + k_{isc}^T + k_q[Q]\}[T_1]$$

$$[T_1] = \frac{k_{isc}^{S}[S_1]}{k_p + k_{isc}^{T} + k_q[Q]}$$

By putting value of [S₁] from equation (12.51) in above equation

$$[T_1] = \frac{k_{isc}^{S}}{k_p + k_{isc}^{T} + k_q[Q]} \cdot \frac{I_a}{k_{ic} + k_f + k_{isc}^{s}}$$

Putting value of [T₁] in equation (12.50), we get

$$\phi_p = \frac{k_p}{I_a} \cdot \frac{k_{isc}^{S}}{k_p + k_{isc}^{T} + k_q[Q]} \cdot \frac{I_a}{k_{ic} + k_f + k_{isc}^{s}}$$

$$\phi_p = \frac{k_p k_{isc}^{S}}{\left(k_{ic} + k_f + k_{isc}^{s}\right)\left(k_p + k_{isc}^{T} + k_q[Q]\right)} \qquad (12.52)$$

Dividing equation (12.52) by (12.46), we get

$$\frac{\phi_p}{\phi_p^o} = \frac{k_p k_{isc}^{S}}{\left(k_{ic} + k_f + k_{isc}^{s}\right)\left(k_p + k_{isc}^{T} + k_q[Q]\right)} \cdot \frac{\left(k_p + k_{isc}^{T}\right)\left(k_f + k_{ic} + k_{isc}^{s}\right)}{k_p k_{isc}^{s}}$$

$$\frac{\phi_p}{\phi_p^o} = \frac{k_p + k_{isc}^{T}}{k_p + k_{isc}^{T} + k_q[Q]}$$

$$\frac{\phi_p^o}{\phi_p} = \frac{k_p + k_{isc}^{T} + k_q[Q]}{k_p + k_{isc}^{T}}$$

$$\frac{\phi_p^o}{\phi_p} = 1 + \frac{k_q}{k_p + k_{isc}^{T}}[Q]$$

$$\frac{\phi_p^o}{\phi_p} = 1 + k_q \tau_p^o [Q] \qquad (12.53)$$

This equation is called Stern-Volmer equation for phosphorescence quenching. The rate of the intensity (I_p^o) of phosphorescence in the absence of quencher to the intensity (I_p) of phosphorescence in the presence of quencher is proportional to the ratio of the quantum yields so above equation can be written as

$$\frac{I_p^o}{I_p} = 1 + k_q \tau_p^o [Q] \qquad (12.54)$$

12.11 THE PHOTOCHEMICAL REACTION BETWEEN BROMINE AND HYDROGEN

The chemical reaction between hydrogen and bromine gives hydrogen bromide. The reaction can be initiated by heating or irradiation process. Mechanism of thermal reaction is described in chapter 5. In this section we shell discuss kinetics and mechanism of this reaction initiated by light absorption. Initiation step in photochemical reaction is different from that of the thermal reaction. Chain propagation and termination steps are same in both cases. In thermal reaction initiation step is thermal decomposition of bromine molecule into bromine radicals while in photochemical reaction the initiation step is dissociation of bromine molecule as a result of absorption of light of sufficiently short wavelength. The quantum yield of this reaction is 0.01.

The overall reaction can be written as

$$H_2 + Br_2 \xrightarrow{h\upsilon} 2HBr$$

The experimental rate law expression for the above reaction was found to be

$$\frac{d[HBr]}{dt} = \frac{k[H_2]I^{1/2}}{1 + k'\frac{[HBr]}{[Br_2]}} \qquad (12.55)$$

Where k and k′ are constants and I is intensity of absorbed light (expressed in Einstein dm^{-3}s^{-1}). The mechanism of the above reaction is given below:

a) $Br_2 \xrightarrow[h\upsilon]{k_1} Br^{\bullet} + Br^{\bullet}$ (Initiation)

b) $Br^{\bullet} + H_2 \xrightarrow{k_2} HBr + H^{\bullet}$

c) $H^{\bullet} + Br_2 \xrightarrow{k_3} HBr + Br^{\bullet}$

d) $H^{\bullet} + HBr \xrightarrow{k_4} H_2 + Br^{\bullet}$ (Propagation)

e) $Br^{\bullet} + Br^{\bullet} \xrightarrow{k_5} Br_2$ (Termination)

The rate of formation of HBr from the above mechanism can be written as

$$\frac{d[HBr]}{dt} = k_2[Br^{\bullet}][H_2] + k_3[Br_2][H^{\bullet}] - k_4[H^{\bullet}][HBr]$$

$$d[HBr] = k_2[Br^{\bullet}][H_2] + \{k_3[Br_2] - k_4[HBr]\}[H^{\bullet}] \qquad (12.56)$$

The concentration of $Br^{\bullet}$ and $H^{\bullet}$ can be determined using steady state approximation. From above mechanism rate of formation of bromine radical can be written as

$$\frac{d[Br^{\bullet}]}{dt} = 2k_1 I - k_2[Br^{\bullet}][H_2] + k_3[H^{\bullet}][Br_2] + k_4[HBr][H^{\bullet}] - 2k_5[Br^{\bullet}]^2$$

$$0 = 2k_1 I - k_2[Br^{\bullet}][H_2] + k_3[H^{\bullet}][Br_2] + k_4[HBr][H^{\bullet}] - 2k_5[Br^{\bullet}]^2$$

$$k_2[Br^{\bullet}][H_2] + 2k_5[Br^{\bullet}]^2 = 2k_1 I + k_3[H^{\bullet}][Br_2] + k_4[HBr][H^{\bullet}]$$

$$k_2[Br^{\bullet}][H_2] + 2k_5[Br^{\bullet}]^2 = 2k_1 I + \{k_3[Br_2] + k_4[HBr]\}[H^{\bullet}] \qquad (12.57)$$

Two unknown quantities i.e. $\left[H^\bullet\right]$ and $\left[Br^\bullet\right]$ are still present in equation (12.57), so we cannot evaluate the value of one quantity without knowing the other.

Applying steady state approximation on rate of formation of hydrogen radical we can get the expression for concentration of hydrogen radical as

$$d[H^\bullet]/dt = k_2[Br^\bullet][H_2] - k_3[H^\bullet][Br_2] - k_4[HBr][H^\bullet]$$

$$0 = k_2[Br^\bullet][H_2] - k_3[H^\bullet][Br_2] - k_4[HBr][H^\bullet]$$

$$k_2[Br^\bullet][H_2] = \{k_3[Br_2] + k_4[HBr\}[H^\bullet]$$

$$[H^\bullet] = \frac{k_2[Br^\bullet][H_2]}{\{k_3[Br_2] + k_4[HBr\}} \qquad (12.58)$$

By putting the value of hydrogen radical concentration from equation (12.58) into equation (12.57) we get

$$k_2[Br^\bullet][H_2] + 2k_5[Br^\bullet]^2 = 2k_1\,I + \{k_3[Br_2] + k_4[HBr]\}\{\frac{k_2[Br^\bullet][H_2]}{\{k_3[Br_2] + k_4[HBr\}}\}$$

$$k_2[Br^\bullet][H_2] + 2k_5[Br^\bullet]^2 = 2k_1 I + k_2[Br^\bullet][H_2]$$

$$2k_5[Br^\bullet]^2 = 2k_1 I$$

$$k_5[Br^\bullet]^2 = k_1 I$$

$$[Br^\bullet]^2 = (\frac{k_1}{k_5})I$$

$$[Br^\bullet] = (\frac{k_1}{k_5})^{1/2} I^{1/2} \qquad (12.59)$$

By putting the value of $\left[Br^\bullet\right]$ into the equation (12.58) from (12.59) we get

$$[H^\bullet] = \frac{k_2(\frac{k_1}{k_5})^{1/2} I^{1/2}[H_2]}{k_3[Br_2] + k_4[HBr]} \qquad (12.60)$$

By putting the value of $\left[Br^\bullet\right]$ and $\left[H^\bullet\right]$ from equation (12.59) and (12.60) into equation (12.56), we get expression for rate of formation of HBr in term of concentration of Br2, HBr, H2 and intensity of the light absorbed.

$$\frac{d[HBr]}{dt} = k_2[H_2](\frac{k_1}{k_5})^{1/2} I^{1/2} + \{k_3[Br_2] - k_4[HBr]\}\{\frac{k_2(\frac{1}{k_5})^{1/2} I^{1/2}[H_2]}{k_3[Br_2] + k_4[HBr]}\}$$

$$\frac{d[HBr]}{dt} = k_2(\frac{k_1}{k_5})^{1/2} I^{1/2}[H_2]\{1 + \frac{k_3[Br_2] - k_4[HBr]}{k_3[Br_2] + k_4[HBr]_2}]$$

$$\frac{d[HBr]}{dt} = k_2\left(\frac{k_1}{k_5}\right)^{1/2} I^{1/2} \frac{[H_2]2k_3[Br_2]}{k_3[Br_2] + k_4[HBr]}$$

Divide numerator and denominator by $k_3[Br_2]$

$$\frac{d[HBr]}{dt} = 2k_2\left(\frac{k_1}{k_5}\right)^{1/2} I^{1/2} \frac{[H_2]}{1 + \frac{k_4}{k_3}\frac{[HBr]}{[Br_2]}}$$

$$\frac{d[HBr]}{dt} = \frac{kI^{1/2}[H_2]}{1 + k'\frac{[HBr]}{[Br_2]}} \qquad (12.61)$$

Where, $k = 2k_2\left(\frac{k_1}{k_5}\right)^{1/2}$

And $k' = \frac{k_4}{k_3}$

Expression (12.61) is same as given in equation (12.55).

12.12 THE PHOTOCHEMICAL REACTION BETWEEN HYDROGEN AND CHLORINE

The chemical reaction between hydrogen and chlorine in the presence of light produces hydrogen chloride with explosion. In 1930, Bodenstein and Hanger investigated the kinetics of this photochemical reaction. The rate law expression for the reaction on the basis of their experimental observation is given below

$$d[HCl]/dt = kI_a[H_2] \qquad \beta = 10^4 - 10^6 \qquad (12.62)$$

Where I_a is the rate of absorption of light in Einstein $dm^{-3}s^{-1}$. They proposed the following mechanism for the reaction.

a) $Cl_2 \xrightarrow[k_1]{h\upsilon} 2Cl^{\bullet}$ (i)

b) $Cl^{\bullet} + H_2 \xrightarrow{k_2} HCl + H^{\bullet}$ (ii)

c) $H^{\bullet} + Cl_2 \xrightarrow{k_3} HCl + Cl^{\bullet}$ (iii)

d) $Cl^{\bullet} \xrightarrow{k_1} \frac{1}{2}Cl_2$ (iv)

In the above mechanism, step (i) is initiation and it is a photochemical process. The chlorine radical produced in initiation step reacts with hydrogen molecule to produce HCl and hydrogen radical which reacts with chlorine molecule to generate HCl and chlorine radicals. The combination of chlorine radical is a termination step. The above mechanism was suggested in the absence of impurities like oxygen for equimolar quantities of hydrogen and chlorine. The net rate of reaction in term of rate of formation of HCl according to above mechanism, can be written as

$$d[HCl]/dt = k_2[Cl^\bullet][H_2] + k_3[Cl_2][H^\bullet] \qquad (12.63)$$

Hydrogen and chlorine radical concentration are two unknown quantities in the above expression and their value can be determined using steady state approximation.

Hence net rate of formation of chlorine radical is

$$d[Cl^\bullet]/dt = 2I_a - k_2[Cl^\bullet][H_2] + k_3[Cl_2][H^\bullet] - k_4[Cl^\bullet]$$

Applying steady state approximation

$$0 = 2I_a + k_3[Cl_2][H^\bullet] - \{k_2[H_2] + k_4\}[Cl^\bullet]$$

$$k_2[H_2][Cl^\bullet] + k_4[Cl^\bullet] = 2I_a + k_3[Cl_2][H^\bullet] \qquad (12.64)$$

Similarly, net rate of formation of hydrogen radical is

$$d[H^\bullet]/dt = k_2[H_2][Cl^\bullet] - k_3[Cl_2][H^\bullet]$$

$$k_2[H_2][Cl^\bullet] = k_3[Cl_2][H^\bullet] \qquad (12.65)$$

Subtracting equation (12.65) from equation (12.64), we get

$$k_4[Cl^\bullet] = 2I_a$$

$$[Cl^\bullet] = 2I_a / k_4 \qquad (12.66)$$

By putting the value of $\left[Cl^\bullet\right]$ from equation (12.66) into equation (12.65), we get

$$k_2(2I_a / k_4)[H_2] = k_3[Cl_2][H^\bullet]$$

$$[H^\bullet] = k_2(2I_a)[H_2] / k_3k_4[Cl_2] \qquad (12.67)$$

Equation (12.67) gives concentration of hydrogen radical in term of concentration of H_2 and Cl_2 and rate of absorption of light.

By putting the value of $\left[Cl^\bullet\right]$ and $\left[H^\bullet\right]$ from equation (12.66) and (12.67) respectively into equation (12.63), we get

$$d[HCl]/dt = k_2(2I_a / k_4)[H_2] + k_3[Cl_2]k_2(2I_a)[H_2] / k_3k_4[Cl_2]$$

$$d[HCl]/dt = k_2(2I_a / k_4)[H_2] + k_2(2I_a / k_4)[H_2]$$

$$d[HCl]/dt = 4k_2(I_a / k_4)[H_2]$$

$$d[HCl]/dt = (4k_2 / k_4)I_a[H_2]$$

$$d[HCl]/dt = kI_a[H_2]$$

Where $k = (4k_2 / k_4)$

Hence rate of reaction depends upon rate of absorption of radiation and concentration of hydrogen. The above expression is similar as given in equation (12.62).

Comparison between photochemical formation of HBr and HCl

Differences

(i) The regeneration of Cl atom in step c (of mechanism of photochemical formation of HCl) after the formation of two molecules of HCl, continues the propagation reaction and a large number of molecules of HCl are formed. While the regeneration of the Br atom does not continue the chain reaction.

(ii) Reaction in step b (of mechanism of photochemical formation of HCl) is very fast. Activation energy (E_a) for steps b & c is 5kcal/mol and easily available in the reaction. While on the other hand, in step b (of mechanism of photochemical formation of HBr) is very slow and depends upon the temperature. E_a is 18kcal/mol and not easily available in the reaction.

(iii) Step b (of mechanism of photochemical formation of HCl) is not reversible but step b (of mechanism of photochemical formation of HBr) is reversible reaction.

(iv) Termination reaction (of mechanism of photochemical formation of HCl) can take place on the wall of the reaction vessel as well as in gas phase. While in (mechanism of photochemical formation of HBr) termination reaction does not take place on the wall of the vessel.

(v) The quantum yield in formation of HCl has been found 10^4-10^6 while in the case of formation of HBr quantum yield is 0.01.

Similarities

(i) First step (of mechanism of photochemical formation of HCl) is dissociation of Cl_2 into $2Cl^\cdot$ by absorption of light. While in (mechanism of photochemic-al formation of HBr) first step is the dissociation of Br_2 into $2Br^\cdot$ by abso-ption of light.

(ii) In both cases termination takes place between two similar atoms.

(iii) In formation of HCl, rate law expression is

$$\frac{d[HCl]}{dt} = k[H_2]I_{abs}^{1/2}$$

$$\frac{d[HCl]}{dt} = k[H_2]I_{abs}$$

While in case of formation of HBr, rate law expression is

$$\frac{d[HBr]}{dt} = \frac{k'[H_2]I_{abs}^{1/2}}{1 + \frac{k''[HBr]}{[Br_2]}}$$

12.13 PHOTOCHEMICAL DECOMPOSITION OF HI

The above reactions deal with photochemical reactions between halogens and hydrogen. Photochemical decomposition of hydrogen halides has also been reported in scientific literature. For example photochemical decomposition of hydrogen iodide (HI) has been studied by a German physical chemist by Emil Gabriel Warburg (1845-1931) who found that this photochemical reaction has quantum yield equals to 2; that is two molecules of hydrogen iodide are converted into H_2 and I_2 when one photon is absorbed. On the basis of this finding, he proposed the following simple mechanism:

a- $HI \xrightarrow{h\upsilon} H^{\bullet} + I^{\bullet}$

b- $HI + H^{\bullet} \rightarrow H_2 + I^{\bullet}$

c- $I^{\bullet} + I^{\bullet} \rightarrow I_2$

On the addition of all above reactions, we get overall reaction as:

$$2HI \xrightarrow{h\upsilon} H_2 + I_2$$

The above reaction is not a chain reaction.

12.14 PHOTOCHEMICAL DECOMPOSITION OF ACETALDEHYDE

Kinetics of thermal decomposition of acetaldehyde has been discussed in chapter 5. Acetaldehyde can be decomposed into methane, carbon monoxide, ethane and some other minor products by photochemical reaction. The photochemical decomposition of acetaldehyde is also known as photolysis of acetaldehyde. The overall reaction of photolysis of acetaldehyde can be written as

$$\mathrm{CH_3CHO + h\nu \rightarrow CH_4 + CO + C_2H_6 + others}$$

Kinetics and mechanism of photolysis of acetaldehyde is given below:

$\mathrm{CH_3CHO + h\nu \xrightarrow{k_1} CH_3 + CHO}$ (Initiation) Rate = $k_1 I_a$

$\mathrm{CH_3 + CH_3CHO \xrightarrow{k_2} CH_4 + CH_3CO}$ (Propagation) Rate = $k_2[CH_3][CH_3CHO]$

$\mathrm{CH_3CO \xrightarrow{k_3} CO + CH_3}$ (Propagation) Rate = $k_3[CH_3CO]$

$\mathrm{CH_3 + CH_3 \xrightarrow{k_4} C_2H_6}$ (Termination) Rate = $-\frac{1}{2}\frac{d[CH_3]}{dt} = k_4[CH_3]^2$

According to above mechanism, rate of reaction can be written in term of rate of formation of CO as

$$\frac{d[CO]}{dt} = k_3[CH_3CO] \qquad (12.68)$$

In the above expression CH_3CO is reaction intermediate and its concentration is not a measurable quantity. In order to find its concentration in terms of concentration of reactants or products, steady state approximation can be applied on CH_3CO. So according to steady state approximation, net rate of formation of CH_3CO will be equal to zero.

$$0 = k_2[CH_3][CH_3CHO] - k_3[CH_3CO] \qquad (12.69)$$

By rearranging equation (12.69) , we get

$$k_3[CH_3CO] = k_2[CH_3][CH_3CHO]$$

$$[CH_3CO] = k_2 / k_3[CH_3][CH_3CHO] \qquad (12.70)$$

Equation 12.70 gives concentration of CH_3CO in terms of concentration of CH_3 and CH_3CHO. In this expression $[CH_3]$ is still unknown quantity. In order to find the expression for concentration of CH_3CO, we have to find the concentration of CH_3 in terms of measureable quantities. CH_3 is also reaction intermediate. So according to steady state approximation net rate of formation of CH_3CO will be equal to zero.

$$0 = k_1I_a - k_2[CH_3][CH_3CHO] + k_3[CH_3CO] - 2k_4[CH_3]^2 \quad (12.71)$$

By adding equation 12.69 and 12.71, we get

$$0 = k_1I_{abs} - 2k_4[CH_3]^2$$

$$2k_4[CH_3]^2 = k_1I_{abs}$$

$$[CH_3]^2 = k_1I_{abs} / 2k_4$$

$$[CH_3] = (k_1I_{abs} / 2k_4)^{1/2} \qquad (12.72)$$

By putting values $[CH_3]$ from equation 12.72 into equation 12.70, we get

$$[CH_3\,CO] = \frac{k_2}{k_3}\left(\frac{k_1I_a}{2k_4}\right)^{1/2}[CH_3CHO] \qquad (12.73)$$

Equation 12.73 gives concentration of $[CH_3\,CO]$ in terms of concentration of $[CH_3\,CHO]$. By putting the values of $[CH_3\,CO]$ from equation 12.73 into 12.68, we get

$$\frac{d[CO]}{dt} = k_3\frac{k_2}{k_3}(\left(\frac{k_1I_a}{2k_4}\right)^{1/2}[CH_3CHO]$$

$$\frac{d[CO]}{dt} = K_2\left(\frac{k_1I_a}{2k_4}\right)^{1/2}[CH_3CHO]$$

$$\frac{d[CO]}{dt} = k(I_a)^{1/2}[CH_3CHO] \qquad (12.74)$$

Where $k = k_2\left(\frac{k_1}{2k_4}\right)^{1/2}$

The value of quantum yield can be obtained by dividing rate of formation of CO by the intensity of absorbed radiation as

$$\text{Quantum yield} = \frac{d[CO]}{dt} / I_a$$

$$= \frac{k(I_a)^{1/2}[CH_3CHO]}{I_a}$$

$$\text{Quantum yield} = \frac{k[CH_3CHO]}{I_a^{1/2}} \qquad (12.75)$$

So rate of reaction increases with increase of intensity of light radiation but quantum yield decrease with increase of intensity of light radiation absorbed. However both rate of formation of CO and quantum yield increases with increase of conc of CH_3CHO as given in equation 12.74 and 12.75.

12.15 FLASH PHOTOLYSIS

This technique was developed by Norrish and Porter in 1950. They used an intense flash of light to produce transient species, radicals or excited molecules in concentration that may be four or five order of magnitude greater than found in conventional systems. In ordinary photochemical studies, the light enters the system continuously but at a relatively low intensity level. As a result, the concentration of short lived intermediates is very low and their observation is difficult. In flash photolysis, on the other hand, the system is exposed to a very powerful beam of light for a very short period of time, say few microseconds. This short time duration allows kinetic studies in the microsecond –millisecond region which embraces wide range of radical reactions and energy transfer processes. The powerful light flash produces a much higher concentration of intermediates, such as atoms or free radicals whose concentration and state can be ascertained by continuous observation of their absorption spectra. From such data it is possible to identify these intermediates, to obtain their concentration and even to evaluate in certain instances the rate constants of photochemical reaction steps involving the species. In this technique, light pulses as short as 10 femtosecond (10 fs=10^{-14}s) in the visible region of electromagnetic spectrum are available such that reaction dynamics on this extremely short or ultrafast time scale can be studied. For references, a 3000 cm^{-1} vibrational mode has a period of 10fs (approximately). Therefore reactions can be initiated on same time scale as vibrational molecular motion and this capability has opened up many exciting fields in chemical kinetics.

This capability has been used to determine the ultrafast reaction kinetics associated with vision, photosynthesis, atmospheric processes and charge carrier dynamics in semi conductors. Short optical pulses can be used to perform vibrational spectroscopic measurements (IR or Raman) on 100 fs time scale. Finally NMR techniques as well as optical absorption and vibrational spectroscopy can be used to study reactions that occur on microsecond (10^{-6}s) and longer time scale.

The apparatus for a flash photolysis experiment is shown in Fig.12.9. The reactive materials are irradiated with an intense flash of white light which provides a continuum of wavelengths from infrared to vacuum ultraviolet. The energy for the flash is the energy stored in a large capacitor (10μF) charged to about 10 kV. When the capacitor is discharged through a tube containing an inert gas (such as krypton) at about 100 nm pressure, a brilliant flash of light is produced. This intense light falling on the system raises the material to a variety of excited states and produces a variety of active intermediates. The duration of flash ranges from 1 to 100 μs after the system is exposed to the flash, a time delay circuit fires a low-energy flash from the source or monitoring flash tube. This beam of light passes through the excited species produced by the first flash and an absorption spectrum is recorded. The oscilloscope sweep in Fig12.9 is triggered by a photoelectric cell that detects light from the flash.

By varying the delay time, we can observe the rate of decay of various species. Alternatively, after making an initial spectrographic study to determine the identity of species present, we can choose a particular wavelength and measure the absorption at this wavelength as a function of time; we do this by replacing the monitoring flash tube with a continuum source such as tungsten filament lamp. When we place a mono-chromater in the optical path, the transmitted radiation is collected in a phototube that's out put we can monitor on an oscilloscope. By this means we can follow the concentration of a selected species as a function of time. With a flash lamp, the light flash lasts about 10 μs. Use of laser instead of flash lamp typically gives a pulse of 10ns duration (1ns= 10^{-9}s). With special techniques, we can generate a laser light pulse with short duration of 0.1ps (1ps= 10^{-12}s), allowing rate processes in the picoseconds range to be studied.

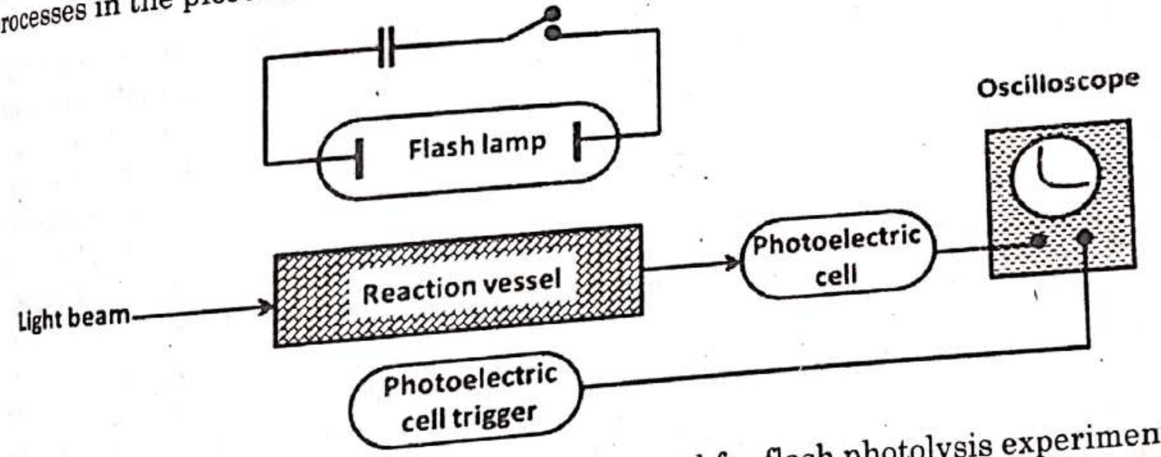


Fig. 12.9 Pictorial diagram of the apparatus used for flash photolysis experiment

12.16 CHEMILUMINESCENCE

"The process of emission of cold visible light as a result of chemical reaction is called *chemiluminescence*". It is a reverse of photochemical reaction. In a photochemical reaction, reactant absorbs light and get excited then goes into product through activation by light absorption but in chemiluminescence, one of the product formed is in excited state. This product comes to ground state by emission of radiations. A general scheme for chemiluminescence is given below

$$A \longrightarrow B^{*} \text{ (Product in electronically excited state)} \qquad \text{(i)}$$

$$B^{*} \longrightarrow B \text{ (Product in ground state)} + h\nu \qquad \text{(ii)}$$

In above scheme, reactant A is converted into product B in its excited state (B*) and then B* emits light (hυ) to produce product B in its ground state. In this way chemical energy is converted into light energy. Some living organisms emit light and show phenomenon of chemiluminescence is known as bioluminescence. For example oxidation of protein, luciferin by atmospheric oxygen in the presence of enzyme luciferase produces cold lights which can b seen by naked eye in fire fly. The chemiluminescence occurring in living organisms is called *bioluminescence*. In other words, bioluminescence is the emission of visible light as a result of a chemical reaction catalyzed by enzyme in living organisms. Chemical reaction between NO and O_3 generates NO_2 in its excited state and O_2 in its ground state. NO_2^* is converted into NO_2 by emission of light in the range of wavelength of 600-2800 nm as given below

$$NO + O_3 \longrightarrow NO_2^{*} + O_2$$

$$NO_2^{*} \longrightarrow NO_2 + h\upsilon \qquad (600\text{–}2800\ \text{nm})$$

Chemiluminescence can be used as an analytical tool to determine the concentration of unknown substance because the rate of light output is directly related to amount of light emitted and accordingly proportional to the concentration of the luminescent material present. This technique is called luminometry.

12.17 PHOTOSENSITIZED REACTION

There are some molecules which do not absorb light energy which is required for a chemical reaction of those molecules. They do not undergo a photochemical reaction. When a foreign substance is added in the reaction mixture, then these reactants can be converted into products in the presence of light. This foreign substance is called *photosensitizer*, these reactions are called photosensitized reactions and the process is called photosensitization. Photosensitization is commonly involved in polymer chemistry in reactions such as photo-polymerization, photo-crosslinking, and photo-degradation. Photosensitizers are also used to generate triplet excited states in organic molecules for photo-catalysis and photodynamic therapy. Photosensitizers generally absorb ultraviolet or visible region of electromagnetic radiation and transfer it to adjacent light in-sensitive molecules. Photosensitizers usually have large de-localized π systems, which lower the energy of HOMO orbitals and its absorption of light might be able to ionize the molecule. There are also examples of using semiconductor quantum dots as photosensitizers. Photosensitization is a key part of Photodynamic therapy (PDT) which is used to treat some cancers. Photosensitization produces singlet oxygen to damage tumors. Photosensitizers are not usually consumed during photosensitization reactions. They return to their original state once the photosensitization reaction is complete. In such cases, role of photosensitizers is similar to catalyst as they do involve in reaction and retain their chemical identity after completion of the reaction. Photosensitizers can be photobleached, a chemical reaction following the absorption of light that produces a different molecular form, which does not absorb light, but this process typically *competes* with the photosensitization reaction. Detail of such cases is beyond the scope of this chapter.

Mechanism of Photosensitization

A photosensitizer absorbs light becomes excited and then pass on this energy to one of the reactants to activate it without itself taking part in the reaction. Hence, photosensitizer acts as an energy carrier. The role of photosensitizer in photosensitized reaction is similar to that of catalyst in thermal reactions. A general mechanism of a photosensitized reaction can be written as

$$P + h\upsilon \longrightarrow P^*$$

In above scheme, P is the photosensitizer in ground state and P* is the photosensitizer in excited state.

$$P^* + S \longrightarrow S^* + P$$

Where S is the reactant in ground state and S* is the substrate or reactant in excited state.

$$S^* \longrightarrow \text{Products}$$

Examples of Photosensitized Reaction

1. H_2 gas undergoes dissociation in the presence of light when Hg vapors are present in the reaction mixture according to this scheme.

$$Hg + H_2 \longrightarrow 2H + Hg$$

Mechanism of this reaction is

$$Hg + h\upsilon \longrightarrow Hg^* \text{ (Excitation of Hg)}$$

$$Hg^* + H_2 \longrightarrow H_2^* + Hg \text{ (Energy transfer)}$$

$$H_2^* \longrightarrow 2H \text{ (Chemical reaction)}$$

2. Chlorophyll acts as photosensitizer in photosynthesis of carbohydrates from a chemical reaction of CO_2 and H_2O in the presence of light as

$$\text{Chlorophyll} + h\upsilon \longrightarrow \text{Chlorophyll}^*$$

$$\text{Chlorophyll}^* + CO_2 \longrightarrow CO_2^* + \text{Chlorophyll}$$

$$6CO_2^* + 6H_2O \longrightarrow C_6H_{12}O_6 + 6O_2$$

12.18 LASERS

The term laser stands for "Light Amplification by Stimulated Emission of Radiation". Laser is a device which produces a highly intense, coherent, monochromatic and unidirectional beam of light.

Principle of Laser

Production of laser can be explained by understanding pumping, spontaneous emission and stimulated emission

(i) Pumping

First process is pumping. During pumping, electric discharge, intense radiations or electric current is passed through lasing medium. These agents cause excitation of electrons to electronic and vibrational energy levels of high energy. Thus excited states become more populated as compared to ground state by pumping as shown in Fig. 12.10 where E_x' becomes populated as compared to E_o due to pumping energy. Electrons are unstable in excited states as compared to ground states. Their life time is 10^{-13}-10^{-15} seconds in excited states. So electrons jump to relatively stable excited states called metastable states E_x (life time = 10^{-3} seconds) by releasing undetectable amount of heat.

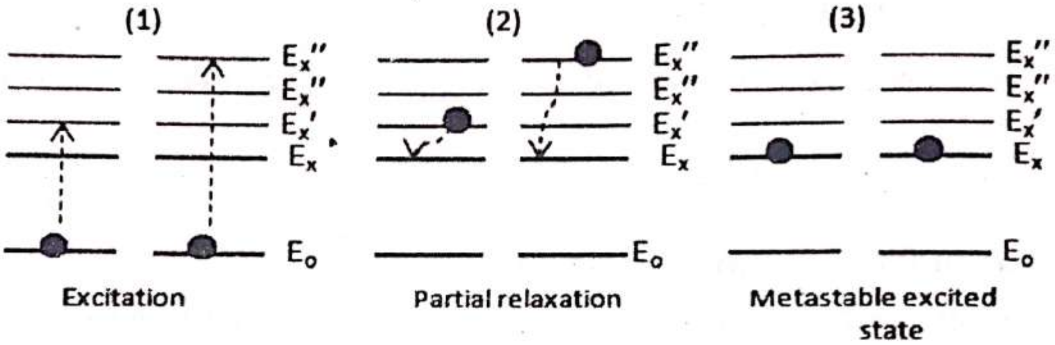


Fig. 12.10 Pumping or excitation

(ii) Spontaneous Emission

Some species in excited state may lose energy equal to $E_x - E_o$ by spontaneous emission. All excited molecules may not lose energy at same time. Moreover orientation of all excited molecules is not same also. So, spontaneous emission is a random process. Photons produced by spontaneous emission have phase difference and travel in different directions, thus they are termed incoherent (Fig.12.11).

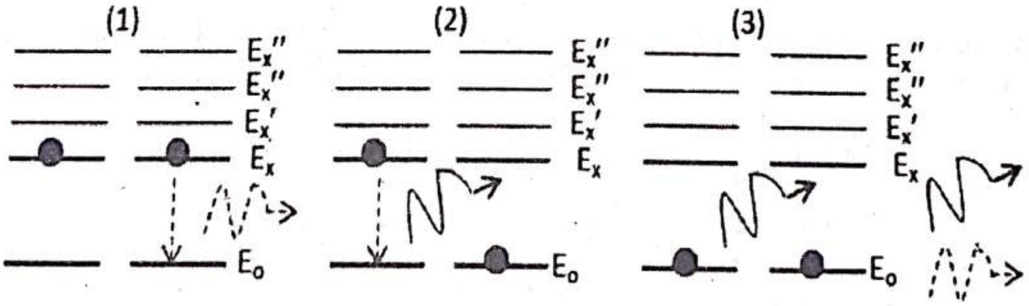


Fig. 12.11 Spontaneous emission

(iii) Stimulated Emission

Photons produced in previous step are struck up by other species in excited state. Photons induce them to lose energy immediately. Thus all atoms get de-excited and produce such photons of equal energy, same phase difference and travelling in similar orientations (Fig. 12.12). Photons produced by stimulated emission get multiplied within very small time and an intense laser beam is produced. Energy of colliding photons is almost equal to the energy of photons produced by stimulated emission.

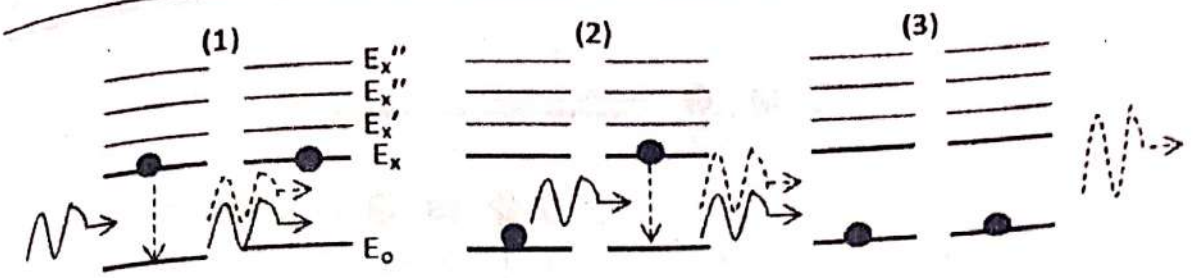


Fig. 12.12 Laser production or stimulated emission

Population Inversion and Light Amplification

In normal population more atoms will reside in the lower energy state than in the excited state. Whereas, a population inversion is that condition, in which higher energy state has a greater population than the lower energy state. Laser action depends on the inversion of the natural excess population in the lower state and then getting the excited state to emit all the excess energy at once. Let us consider three different states at which atoms can reside i.e. E_1 is the ground state, E_2 is the higher energy excited state also named as short lived state and E^* is the metastable state also named as long lived state as shown in Fig. 12.13. A metastable state is an excited state in which an excited electron is unusually stable and electrons spontaneously fall to lower state only after relatively longer time. The transition from or to this state is difficult as compared to other excited states. Hence, instead of direct excitation to metastable state, the electrons are excited to higher energy level. Then, electrons spontaneously fall to metastable state. The incident photons of energy (hf) are used to raise the atoms from the ground state to the excited state but the excited atoms do not decay back to ground state directly. Thus, excited atoms use alternative by decaying spontaneously to metastable state, the atoms reach metastable state much faster than they leave metastable state. This eventually leads to the situation that the metastable state contains more atoms than ground state this situation is known as population inversion. Once the population inversion has been reached, the lasing action of a laser is simple to achieve. The atoms in the metastable state are bombarded by photons of energy (hf) in stimulated emission, giving an intense, coherent beam in the direction of the incident photon. Thus amplification of light is only possible in population inversion. That is why laser production principle is purely based upon population inversion where number of photons lost by absorption is smaller as compared to number of photons produced by stimulated emission. During amplification, one photon induces to give two photons, later two gives four and hence an intense beam is produced. Lasers involve the Boltzmann equation to calculate the populations of energy states.

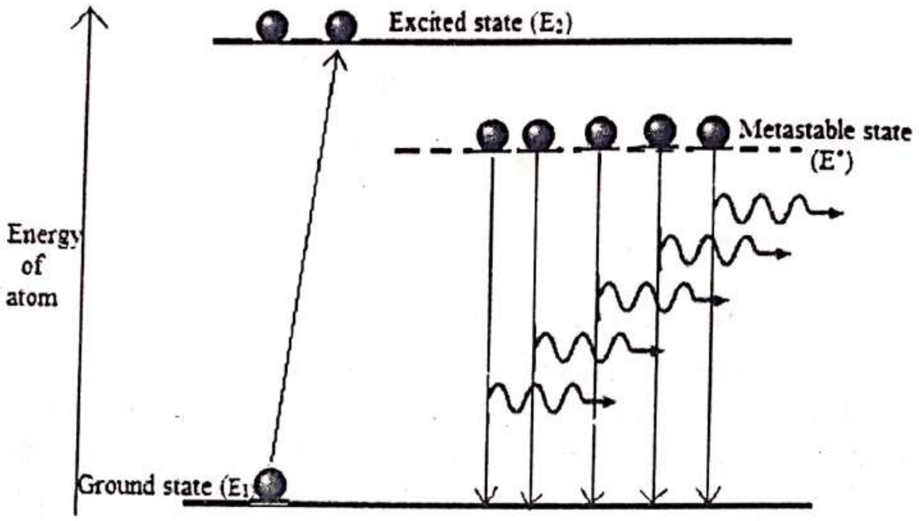


Fig. 12.13 Illustration of population inversion and light amplification

Three and Four Level Systems

Three and four level systems are used for production of laser shown in Fig. 12.14. Electrons jump from ground state E_o to an excited state E_x by pumping. Later they move to a metastable state E_y by radiationless transition. From E_y, molecules jump to E_o and produce laser. This occurs in three level systems where electrons move between three states. Four level system is little different. Here four states are involved. From excited state E_y, molecules jump to another state E_z by emission of photon and then immediately jump back to E_o. Energy of E_z level is greater than that of E_o. Four level systems produces more intense beam because here population inversion attains rapidly by input of small pumping energy.

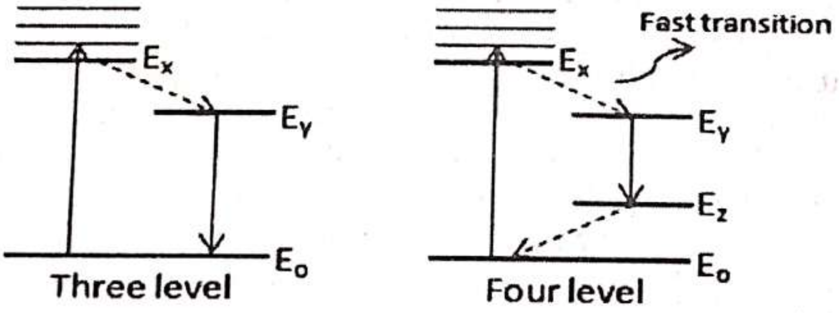


Fig. 12.14 Energy level diagrams of different laser systems

Laser Construction

A laser is constructed from three major parts:

1. An energy source: The energy source is also referred to as pump or pump source. It provides energy to the gain medium to excite it. Electrical discharges, flash lamps, light from some other lasers, chemical reactions or even some explosive devices are used as an energy source depending upon the type of laser. For example He-Ne laser uses electrical discharge as energy source but Excimer laser uses a chemical reaction.

2. Laser medium: Laser medium is also known as gain medium. The gain medium is excited by the pump source to produce a population inversion, and it is the gain medium in which spontaneous and stimulated emission of photons takes place, leading to the phenomenon of optical gain, or amplification. Some dyes in organic solvents are used as a laser medium in liquid lasers. Gases like carbon dioxide, argon and krypton ore mixture of gases like Helium-Neon are used as gain medium in gas lasers.

3. Optical resonator: The optical resonator is also known as optical cavity. It consists of two parallel mirrors placed around the gain medium which provide feedback of the light. The mirrors are given optical coatings to optimize their reflective properties. Typically one mirror is a high reflector, and the other is a partial reflector called output coupler. The output coupler allows some of the light to leave the cavity to produce the laser output beam. Light from the medium, produced by spontaneous emission, is reflected by the mirrors back into the medium, where it may be amplified by stimulated emission. The light may reflect from the mirrors and thus pass through the laser medium many hundreds of times before exiting the optical cavity.

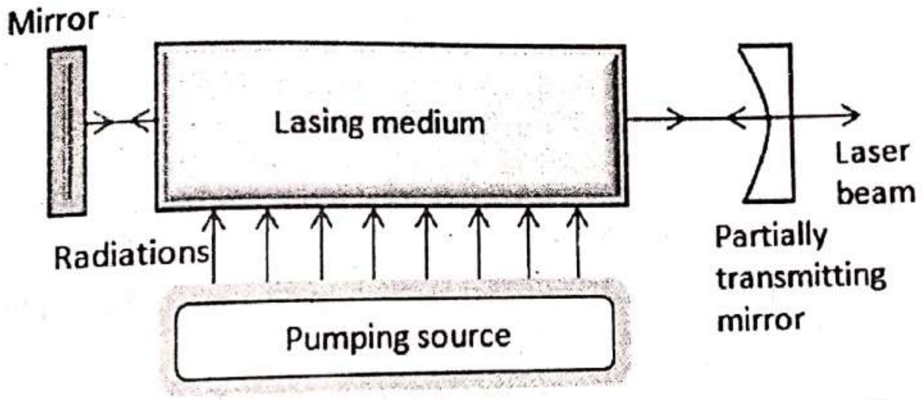


Fig. 12.15 A schematic diagram showing principal components of laser

These principal parts of laser are shown in Fig. 12.15.

Types of Lasers

Lasers can be classified according the following different schemes.

1. On the Basis of Active Media

(a) Gas lasers: active medium used in gas lasers is gas. e. Examples of such kind of laser are He-Ne laser, CO_2 laser and N_2 laser.

(b) Dye lasers: active medium used in these lasers is dye in liquid solvent or in solid.

(c) Solid state lasers: In such kind of laser solid state material is used as an active medium. The semiconductor laser is an example of solid state laser.

(d) Excimer lasers: In these lasers, chlorine or fluorine gas along with an inert gas is used as active medium.

2. On the Basis of Mode of Operation

(a) Continuous wave lasers

(b) Pulsed lasers

3. On the Basis of Number of Metastable Levels in Laser

(a) 3 level lasers

(b) 4 level lasers

Applications of Lasers

Lasers are used in various fields. Applications of lasers in some fields are given below

1. In medicine: lasers are used in surgical treatment, vision treatment, kidney stone treatment, dentistry, hair removal, skin treatment and tattoo removal. Laser beam can be used to remove ulcers in the stomach with very little loss of blood. Because of the burning action of lasers, the cut is also clotted and sealed immediately. The accumulation of red blood cells just under the skin of people appears in the form of red marks, called port wine stains. Laser surgery is done to remove these marks without damaging the outer skin surface and the surrounding blood cells.
2. In the military: lasers are used in missile guidance, radar replacement and target guidance for defense purpose.
3. In electronics: lasers have applications in CDs, DVDs, laser printers, holograms and barcode scanners.
4. Industry: laser beam can be used for cutting, welding and heating various materials.
5. In research: Laser spectroscopy is the branch of spectroscopy which can be used for qualitative and quantitative analysis in scientific research. Laser light scattering is used to characterize polymer and colloidal materials.
6. Environmental science: Lasers are used as environmental monitoring instruments for detection of various pollutants present in the atmosphere.

12.19 PHOTOCHEMISTRY OF VISION

Chemical changes occurring within eye during seeing an object is termed as "photochemistry of vision". An object can be seen only if light coming from the object is focused on retina (Inner layer of eye). The retina is made of the photoreceptor cells, the bipolar cells, ganglion cells, amacrine cells and the horizontal cells. Photoreceptor cells can be classified as rods and cones because of resembling of their shapes with rod and cone geometries. The rods are sensitive to dim light while cones are sensitive to colored light. The light is directed to the photoreceptor cells by the amacrine cells and the horizontal cells. In the retina the photoreceptor cells are connected to the bipolar cells which are in turn connected to the ganglion cells. The ganglion cells are connected to the nerve cells which carry the nerve impulse generated to the occipital lobe of the brain where it is interpreted. Rods are made up of the glycoprotein opsin and a derivative of "Vitamin A" known as the retinals. Retinal is attached with opsin. Before falling the light on retina, retinal has a bent shape and is known as the cis-retinal. When light falls on this cis-retinal, it undergoes isomerization to generate another conformation called trans-retinal. The conversion of cis-retinal to trans-retinal is a photochemical process which initiates further changes inside the eye. Cis trans isomerization resulted from absorption of light is shown in Fig.12.16.

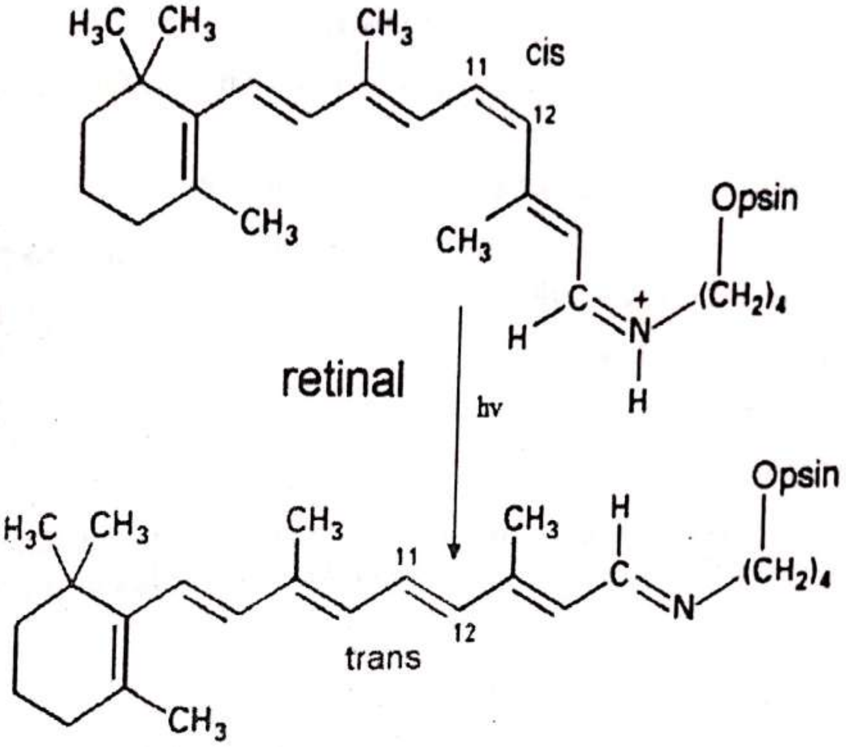


Fig. 32.16: Photochemical Cis-trans transformation of retinal during vision

Due to this cis-trans conversion, the bond between opsin and the trans-retinal is broken. As a result the active site of the opsin molecule becomes free and it may act as catalyst. Thus opsin molecule detached from trans-retinal catalyzes the process of transformation of guanosine diphosphate (GDP) to guanosine triphosphate (GTP). GTP molecule form bond with the alpha subunit attached to the phosphodiesterase and removes it. As a result the phosphodiesterase molecule becomes free. This phosphodiesterase catalyzes the conversion of cyclic guanosine monophosphate (cGMP) molecule into the GMP molecule. This results in the closing of the ion channels and thereby inhibits the movement of the sodium ions into the cell resulting in hyperpolarization. This stops the release of the inhibitory neuro-transmitter and thereby results in the generation of the nerve impulses which is carried to the brain by the nerves for interpretation.

QUESTIONS

Q.1. What are possible relaxation routes for an electronically excited molecule? Elaborate your answer with the help of Jablonski diagram.

Q.2. Define photochemistry and give its applications in daily life.

Q.3. State and explain the laws of photochemistry.

Q.4. What are photochemical reactions and how are they different from thermal reactions?

Q.5. State and Explain Beer-Lambert law and Give its limitations.

Q.6. Give two non-radiative and two radiative deactivation processes of an electronically excited molecule.

Q.7. Write a note on the following

(i) Chemiluminescence

(ii) Photosensitized reactions

Q.8. Give a brief account of photophysical processes. Discuss radiative and non radiative relaxation processes in detail on the basis of Jablonski Diagram.

Q.9. Differentiate the followings

(i) Fluorescence and phosphorescence

(ii) Primary and secondary photochemical reactions

(iii) Absorbance and Molar absorbitivity

Q.10. Define fluorescence life time and fluorescence quantum yield. Derive a mathematical expression for fluorescence life time and fluorescence quantum yield in term of rate constants of various photophysical processes.

Q.11. What is fluorescence quenching? Derive Stern-volmer equation to explain the effect of quencher concentration on rate of fluorescence.

Q.12. What are LASERS? Explain the principle of LASERS productions. Discuss different types of LASERS and their applications.

Q.13. The rate expression for the formation of CCl_4 from photochemical chlorination of chloroform is

$$\frac{d[CCl_4]}{dt} = k[Cl_2]^{1/2} I_a^{1/2}$$

The proposed mechanism for the reaction $Cl_2 + CHCl_3 + h\upsilon \longrightarrow 2Cl$ is

$$Cl_2 + h\upsilon \longrightarrow 2Cl \qquad \text{(i)}$$

$$Cl + CHCl_3 \xrightarrow{k_2} CCl_3 + HCl \qquad \text{(ii)}$$

$$CCl_3 + Cl_2 \xrightarrow{k_3} CCl_4 + Cl \qquad \text{(iii)}$$

$$2CCl_3 + Cl_2 \xrightarrow{k_4} 2CCl_4 \qquad \text{(iv)}$$

Using steady state approximation proves that mechanism is correct.

Q.14. Calculate the energy of photon corresponding to a wavelength of 425 nm. Also calculate the energy of 1 mole of photon corresponding to same wavelength.

(4.67×10^{-19} J, 281 kJmol^{-1})

Q.15. Calculate the value of fluorescence quantum yield for $\tau_f = 2\times10^{-10} s$ and $k_{ic} = 9\times10^7 s^{-1}$ by assuming that rate constants for intersystem crossing and fluorescence quenching are small. (3.98)

Q.16. The production of hydrogen atoms from a hydrogen molecule requires 431.8 kJmol^{-1} Determine the corresponding wavelength in nm. (277.2 nm)

Q.17. If $k_{ic} = 3\times10^5 s^{-1}$, $k_f = 5\times10^6 s^{-1}$ and $k^s_{isc} = 2\times10^9 s^{-1}$ calculate the fluorescence life time and fluorescence quantum yield. (2 ns, 0.01)

Q.18 0.14 mM solution of a compound placed in a cell of path length 1 cm transmits 36% of light intensity. Calculate the molar absorption coefficient of solute. (3.16×10^3 L$mol^{-1}s^{-1}$)

Q.19. Name the following photophysical processes

(i) $S^* \longrightarrow S + h\upsilon$

(ii) $S^* + h\upsilon \longrightarrow S + 2h\upsilon$

(iii) $S^* \longrightarrow T$

(iv) $T^* \longrightarrow S + h\upsilon$

(v) $S^* \longrightarrow S$

Q.20. Write a short note on Flash Photolysis.

Q.21. What is quantum yield? Discuss its significance in photochemistry. Enlist various reasons for low and high quantum yield.

Q.22. Justify/Comment on the following statements

i) Thermal reactions can occur in the presence and absence of light.

ii) Free energy of a photochemical reaction is always positive.

iii) Lambert-Beer law is applicable to dilute solutions only.

iv) In photochemical reactions, light is always one of the reactants.

v) Transmittance has no units.

vi) Quantum yield tells about the mechanism of a chemical reaction.

vii) Internal conversion is a non-radiative process.

viii) Chemiluminescence is a cold light

ix) Phosphorescence occurs between states of different multiplicity

x) LASER is a coherent beam of light

REFERENCES

1. Alberty, R. A. 1983. Physical Chemistry, 6th Edition, John Wiley and Sons, Inc. New York.

2. Peter, A. and D. P. Paula, 2002. Atkin's Physical Chemistry, 7th Edition, Oxford University press, New York.

3. Maron, S. H. and C. F. Prutton, 2000. Principles of Physical Chemistry, 4th Edition, The Macmillan Company collier-Macmillan Limited, London.

4. R.J. Silbey, R.A. Alberty and M.G. Bawendi 2005. Physical chemistry, Wiley, India.

5. Alberty, R.A. 2003. Physical Chemistry, McGraw-Hill Book Company, London.

6. Engel, T. and P. Reid, 2006. Physical chemistry, 1st Edition, Pearson Education, Inc. and Dorling Kindersley Publishing Inc. New Delhi, India.

7. Barrow, G.M. 1997. Physical Chemistry, Mc Graw Hill, Tokyo.

Chapter 13

POLYMER CHEMISTRY

13.1 INTRODUCTION

Polymers are macromolecules which are composed of billions of repeating units. Their vast range of applications has significantly enhanced the attention of scientists towards study of their synthesis and structural analysis.

The structural unit of polymer is its repeating unit. Repeating unit repeats itself in structure thousands of times and fabricates a polymer. Monomers are assembled in a repeating unit. Sometimes repeating unit is made up of a single monomer as in homopolymer, sometimes it is made up of two monomers as in copolymer and sometimes it is made up of three monomers as in terpolymer. Thus number of monomers in a repeating unit may vary. In this way control on monomers, controls repeating unit which in turn control polymer. This is how structure of polymer is managed by proper control at such small level.

There is a vast range of polymers, so many classification schemes are possible. Origin, nature, structure, polarity, homogeneity, functioning, thermosensitivity and many more are used as basis in this chapter for classification of polymers. Polymerization is a complex process which has its own kinetics. Addition and condensation polymers are used nowadays in material science, electronics, plastic industry, textiles, aerospace technology and many more. Thus their yield is monitored by study of their kinetics. Kinetics provides information about ratios of monomers incorporating into the polymer and left in reaction mixture at any time. It helps to estimate reaction completion time without any experimental work. Moreover 100% conversion is also estimated under various sets of reaction conditions. Copolymers are also significantly used nowadays. Study about their classification, models, kinetics and reactivity ratios are also included in this chapter.

All polymeric chains synthesized at same time are not of same mass. Polydispersity exists among them. Number, z, mass and viscosity average molecular weights are normally used to describe molar mass of a polydisperse system of polymer. Many methods like viscometry, osmometry, light scattering, sedimentation and many other methods are explained over here by which different average molar masses of polymers can be measured with accuracy. Analytical method like gel permeation chromatography is also discussed in this chapter by which every molar mass fraction of polymer can be separated and analyzed.

13.2 CLASSIFICATION OF POLYMERS

Different trends of classification of polymers are reported due to vastness of polymers according to their structure, property, origin, sensitivity, physical state, mode of formation and polarity. Thus aforementioned characteristics are used as basis for classification of polymers as shown in Fig. 13.1.

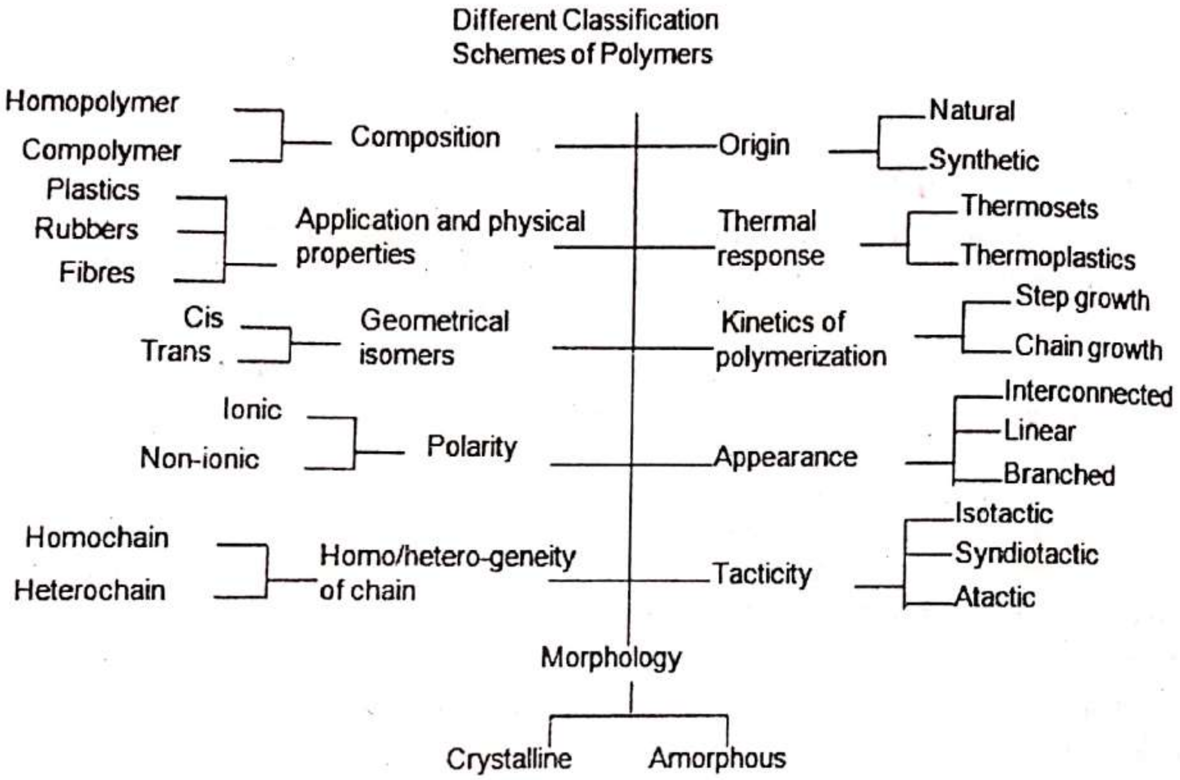


Fig. 13.1 Different classification schemes of polymers

(1) On the Basis of Origin/Occurrence

Natural, synthetic and semi-synthetic are three major divisions of polymers on the basis of their occurrence or origin.

(a) **Natural Polymers:** As name indicates, origin of natural polymers is nature i.e.; animals, plants or rocks. Examples of such polymers are: natural rubber (1, 4-cis-polyisoprene), starch, quartz, proteins, cellulose etc.

(b) **Synthetic Polymers:** Such polymers which are synthesized by man are known as synthetic polymers, e.g.; polystyrene, polyvinyl chloride (PVC), polyester etc.

(c) **Semi-synthetic Polymers:** These are chemically modified natural polymers by man for commercial purposes. Semi-synthetic polymers either have backbone of natural polymers and pendent group of synthetic polymers or their one block is made up of natural polymers and other component is made up of synthetic polymers. Hydrogenated rubber, cellulose nitrate and cellulose acetate are some examples of semi-synthetic polymers.

(2) On the Basis of Kinetics of Polymerization

Addition and condensation polymerization are two basic kinetic mechanisms for formation of polymers.

(a) **Chain Growth Polymers:** Self addition of monomers occurs in addition polymerization (chain growth polymerization). No foreign molecule incorporated in chain during growth of polymer. No side product is formed. Molecular weight of polymer is exactly multiple of molecular weight of monomer. Mostly olefins follow addition polymerization as butadiene gives polybutadiene, styrene gives polystyrene and vinyl chloride gives polyvinylchloride.

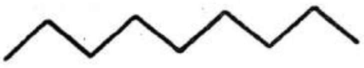
(b) **Step Growth Polymers:** Monomers have functional groups like carboxyl (-COOH) and amino (-NH_2). Two or more than two monomers react in step-wise manner and produced a polymer along with elimination of small molecules. This sort of polymerization is called step growth (condensation) polymerization. Nylon, polyurethane and polyester are some examples of step growth polymers.

(3) On the Basis of Polarity

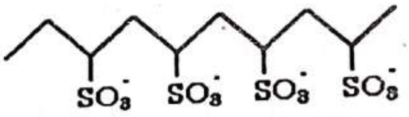
Main chain of polymers or their pendent groups often contain charges. Thus ionic and non-ionic are two categories on the basis of polarity of polymers.

(a) **Non-Ionic Polymers:** Non-ionic polymers have no charge containing moiety in polymer. Polyethylene and polypropylene are two examples of non-ionic polymers.

(b) **Ionic Polymers:** Ionic polymers have charge on pendent groups, as in polymer (sulfonated polyethylene) of ethylene sulfite. These are also known as polyelectrolytes.



Polyethylene



Sulfonated polyethylene

(4) On the Basis of Structure of Polymers

Polymers can be branched or inter-linked, but versatile pattern of branching and interlinking gives a wide range of different polymers.

(a) **Linear Polymers:** A non-branched and straight chain of bonded monomers which has only two ends is called linear polymer. They are mostly synthesized by condensation polymerization. Nylon and polystyrene are linear polymers.

(b) **Branched Polymers:** Sometimes small branches of finite length are attached to main chains of polymers, termed as branched polymers. These branches can be of made up of molecules similar or dissimilar to main chain. Thus branched polymers are further sub-divided into graft copolymer, star polymer, comb-like polymer, dendrimer.

(i) Graft Copolymers: One type of molecules form main chain and other type of molecules form branches on these main chains.

(ii) Star Polymers: Sometimes terminals of many linear polymers join at common point and form star polymers.

(iii) Dendrimers: Dendrimers are tree-like in structure. They have no backbone. Extensive branching perpetuates in such a way which give an unusual structure called dendrimer.

(iv) Comb Polymers: These branched polymers have a backbone over which branches are hanging just like comb.

(c) Crosslinked or Network Polymers: Different chains of polymers get interconnected by covalent bonds and form crosslinked polymers. Point of interconnection is called crosslinking point. Density of crosslinked polymers determine by density of crosslinking points or junctions per unit volume. Crosslinking pattern in network polymers can be two or three dimensional. Thus on the dimensions of crosslinking, network polymers are further subdivided into two categories.

(i) Planar Network Polymer Structures: Two dimensional crosslinking containing polymers are called planar network polymer structures. Graphite is their common example. Ladder polymers are also planar polymers. They have two main chains which are crosslinked just like ladder.

(ii) Space Network Polymer Structures: Three dimensional crosslinked polymers are called space network polymer structures. Diamond is their well known example.

(5) On the Basis of Thermal Behavior

Thermosets and thermoplastics are two types of polymers on the basis of response towards temperature.

(a) Thermosets: Thermosets cannot be softened again and again on heating, once they get solidified. Heating produces chemical reactions which lead towards further growth or crosslinking. Thus these polymers cannot be recycled. Epoxy resins, diene rubbers and unsaturated polyesters are some examples of thermosets.

(b) Thermoplastics: Thermoplastics like polyvinyl chloride, polyethers etc can be softened and solidified again and again on heating and cooling respectively. Heating or cooling does not produce chemical changes in them, so they can be recycled many times.

(6) On the Basis of Tacticity

Polymers having different spatial arrangements of atoms around asymmetric carbon have different properties. This difference in spatial arrangements (configuration) is called tacticity. Tacticity make polymers optically active. Tacticity produces optical isomerism in polymers. Optically active monomers can be R (rectus) or S (sinister) rotatory. Here isomeric polymers differ only in head to tail linkages of optically active monomers. Thus isotactic, syndiotactic and atactic are three different categories of polymers on the basis of pattern of head to tail linkages of repeating units.

(a) **Isotactic:** Isotactic polymers like erythrodiisotactic and threodiisotactic have same configuration of every chiral carbon. Thus isotactic sequence can be represented as *R-R-R-R-R-R* or *S-S-S-S-S-S*. Isotacticity highly favors closest packing of molecules and crystallinity among isotactic, syndiotactic and atactic polymers.

(b) **Syndiotactic:** If dextro and levo rotatory repeating units attach alternatively, then syndiotactic polymer is formed. It is represented as *R-S-R-S-R-S-R*. Erythrodisyndiotactic and threodisyndiotactic are examples of this kind of polymers. These polymers are less crystalline and packed than isotactic polymers.

(c) **Atactic or Heterotactic:** There is no pattern of linkage of two optically active monomers in atactic polymers. Monomers can be linked head to head, tail to tail and head to head for some portion of chain, thus represented as *R-R-R-S-R-S-R-S-S-S-R*. Atacticity hinders crystallinity and packing. Thus they are least crystalline and packed among all three listed types.

(7) On the Basis of Geometrical Isomerism in Polymers

Arrangement of atoms or groups around double bond produces geometrical isomerism in molecules. C is and trans are two basic categories of geometrical isomers.

(a) **Cis Polymers:** If two similar groups are positioned on same side of double bond then cis polymer is formed as cis-1,3-butadiene (synthetic rubber).

(b) **Trans Polymers:** If two similar groups are positioned on opposite side of double bond then trans polymer is formed as trans-1,3-butadiene.

(8) On the Basis of Morphology of Polymers

Amorphous and crystalline are two different kinds of polymers on the basis of their morphology.

(a) **Crystalline Polymers:** Polymers are not completely crystalline rather they are semi-crystalline which have regions of crystalline as well as amorphous polymers. This sort of polymers is characterized by melting point (T_m) at which crystalline phase transform into solid amorphous phase. Thermosets are crystalline polymers while thermoplastics decompose on heating to high temperatures.

(b) **Amorphous Polymers**: Amorphous polymers are characterized by glass transition temperature (T_g) at which hard glass state converted into soft rubbery state.

(9) On the Basis of Application and Physical Properties of Polymers

Rubbers, plastics and fibers are three principle types of polymers on the basis of their physical properties and applications.

(a) **Rubbers:** Rubbers are commonly called elastomers. They are mechanically weak, dimensionally unstable and highly elastic polymers. Their tensile strength lies in range of 300 to 3,000 psi. They have low molecular cohesion. Thus their molecular cohesion is less than 2 Kcal/gmol per 0.5 nm chain length. Rubbers are not highly crosslinked. If they become crosslinked upto desired limit then they become more useful for better applications. Crosslinking of rubber is termed as vulcanization.

(b) **Plastics:** Plastics are dimensionally stable and highly elastic substances. 4,000 to 15,000 psi is range of their tensile strength. They are stronger than rubbers. Plastics exhibit molecular cohesion in range of 2-5 Kcal/gmol per 0.5 nm chain length. They can be soft and flexible or hard and rigid. Phenol-formaldehyde resins, nylon, polyamides, polyvinyl chloride are some examples of common plastics.

(c) **Fibres:** Fibres are strongest among rubbers, plastics and fibres. Their tensile strength lies in range of 20,000 to 150,000 psi. Molecular cohesion of fibres is 4-10 Kcal/gmol per 0.5 nm chain length. Natural and synthetic fibres are largely used in textile, because of their high mechanical strength, thermal insulation, flexibility and softness. Cotton cellulose and silk are natural fibres while polyamides and polyesters are synthetic fibres.

(10) On the Basis of Homo/Heterogeneity of Polymers

Homochain and heterochain polymers are two different types of polymers on the basis of homo/heterogeneity.

(a) **Homochain Polymers:** Such polymers which made up of only one kind of atoms are called homochain polymers, like diamond, graphite, and linear polymers of sulfur and selenium.

(b) **Heterochain Polymers:** Heterochain polymers are made up of more than one kind of atoms. This kind of polymers is more extensively found in list of polymers. Silicones, polyethylene, polyesters, nylon and polyphosphoric acid are some examples of heterochain polymers.

(11) On the Basis of Composition of Polymers

Type of monomer units involved in formation of polymers is the base of classification here. Homopolymer and copolymer are two general kinds on this basis.

(a) **Homopolymers:** Homopolymers are made up of only one kind of monomers, e.g.; polystyrene, polyvinylchloride etc. Interestingly, all homochain polymers are homopolymers but all homopolymers are not homochain polymers.

(b) **Copolymers:** Copolymers are made up of two kinds of monomer units. Nylon and polyesters are copolymers.

Example 13.1

Identify which polymers are formed by addition and which formed by condensation polymerization.

(a) $-(CH_2-CH_2)_n-$ (b) $-(OC-CH_2-CO-NH-CH_2-NH)_n-$

(c) $-(CH-CH(C_6H_5))_n-$ (d) $-(O-CH=CH-O-N-CH=CH-N)_n-$

Solution

(a) and (c) are synthesized by addition polymerization while (b) and (d) are formed by condensation polymerization.

13.3 POLYMERIZATION

Polymerization is a process by which a polymer is synthesized. Route or mechanism of polymerization of different monomers is different. Thus step growth and chain growth are two kinds of kinetic mechanisms of polymerization.

13.4 STEP GROWTH POLYMERIZATION

Polyfunctional monomers polymerize to form step growth polymers. Polyfunctional monomers give a branched polymer as they have more than two reacting sites, while bifunctional monomers give a linear polymer.

Bifunctional monomer-1 HO-A-OH and bifunctional monomer-2 Cl-B-Cl react and initially form HO-A-O-B-Cl along with elimination of hydrochloric acid (HCl). Later HO-A-O-B-Cl reacts with HO-A-OH and yields HO-A-O-B-O-A-OH and HCl. Thus a small molecule of HCl eliminates at every step growth of chain. In this way, polymerization continues and a polymer is formed. General scheme is

$$\underset{\text{Monomer-1}}{HO-A-OH} + \underset{\text{Monomer-2}}{Cl-B-Cl} \rightarrow HO-A-O-B-Cl + HCl$$

$$HO-A-O-B-Cl + HO-A-OH \rightarrow HOAOBOAOH + HCl$$

$$HO-A-O-B-O-A-OH + Cl-B-Cl \rightarrow H(OAOB)_2Cl + HCl$$

$$H(OAOB)_2Cl + xHO-A-OH + xCl-B-Cl \rightarrow \underset{\text{Polymer}}{H(OAOB)_{x+2}Cl} + xHCl$$

Following are some examples of condensation polymerization of some bifunctional monomers.

1. Polyester

$$\underset{\text{1,4-Butanediol}}{HO(CH_2)_2OH} + \underset{\text{Succinic acid}}{HOOC(CH_2)_2COOH} \xrightarrow{-H_2O} HO(CH_2)_2OOC(CH_2)_2COOH$$

$$HO(CH_2)_2OOC(CH_2)_2COOH + nHO(CH_2)_2OH + nHOOC(CH_2)_2COOH$$
$$\xrightarrow{-nH_2O} \underset{\text{Polyester}}{HO\left[(CH_2)_2OOC(CH_2)_2COO\right]_{n+1}H}$$

2. Polyamide

$$\underset{\text{Hexamethylene diamine}}{H_2N(CH_2)_6NH_2} + \underset{\text{Adipic acid}}{HOOC(CH_2)_4COOH} \xrightarrow{-H_2O} H_2N(CH_2)_6HNOC(CH_2)_4COOH$$

$$H_2N(CH_2)_6HNOC(CH_2)_4COOH + nH_2N(CH_2)_6NH_2 + nHOOC(CH_2)_4COOH \xrightarrow{nH_2O} H_2N\left[(CH_2)_6HNOC(CH_2)_4CON\right]_{n+1}H$$

Nylon 6,6 (polyamide)

13.4.1 Characteristics of Step Growth Polymerization

Following are some basic characteristics of step growth polymerization.

(i) This polymer is formed in steps. so small molecules are eliminated during polymerization.

(ii) Equimolecular proportions of both monomers should be used, so that they equally incorporated in polymer, otherwise polymer have that functional group in excess whose monomer was used in greater quantity.

(iii) Non-equimolecular proportions of monomers yield low molecular weight polymer.

(iv) Pure monomers should be used otherwise side reactions may occur and polymer yield decreases.

(v) Reaction between two functional groups depends upon length of chain attached to them in initial stages of reaction. But at later stages, it does not depend upon length of chain.

13.4.2 Kinetics of Step Growth Polymerization

Let esterification of succinic acid with ethylene glycol as an example. This polymerization can be catalyzed and cannot be catalyzed, thus following discussion comprises on kinetics of both types of polymerizations.

(a) In the Absence of Acid Catalyst

Rate of reaction between carboxylic acid and alcohol in the absence of any external catalyst is a third order reaction. Rate of reaction is directly proportional to first power of alcohol concentration and second power of acid concentration, because in the absence of any external acid catalyst, succinic acid itself acts as catalyst and monomer, both at same time. Rate of consumption of –COOH is equal to rate of consumption of –OH.

$$-\frac{d[COOH]}{dt} = -\frac{d[OH]}{dt} \tag{13.1}$$

Rate of consumption of functional group i.e.; –COOH or –OH, is rate of reaction. Thus rate of reaction can be written in terms of rate of consumption of –COOH.

$$-\frac{d[COOH]}{dt} \propto [OH][COOH]^2 \tag{13.2}$$

$$-\frac{d[COOH]}{dt} = k[OH][COOH]^2 \tag{13.3}$$

k is rate constant of reaction. The molar concentration of –OH and –COOH group is equal and can be represented as C.

$$-\frac{dC}{dt} = kC^3$$

So, by separating variables, we get

$$-\frac{dC}{C^3} = kdt \qquad (13.4)$$

By integrating above equation, we get

$$-\int\frac{dC}{C^3} = k\int dt$$

$$-\left[\frac{C^{-3+1}}{-3+1}\right] = kt + c$$

$$\left[\frac{1}{2C^2}\right] = kt + c \qquad (13.5)$$

C is concentration of succinic acid and ethylene glycol at any time while their initial concentration is C₀. Thus on application of boundary conditions, we get

$$\left[\frac{1}{2C_o^2}\right] = c \qquad (13.6)$$

Putting value of c from equation (13.6) into (13.5), we get

$$\frac{1}{2C^2} = kt + \frac{1}{2C_o^2}$$

$$\frac{1}{2C^2} - \frac{1}{2C_o^2} = kt$$

$$\frac{1}{C^2} - \frac{1}{C_o^2} = 2kt$$

$$\frac{1}{C^2} = \frac{1}{C_o^2} + 2kt \qquad (13.7)$$

Equation (13.7) is rate equation for step growth polyesterification. Following are results predicted on the basis of this equation.

(i) This is a straight line equation in intercept form.

(ii) Intercept of the plot obtained from equation (13.7) is equal to inverse of square of initial concentration of monomers.

(iii) Slope is equal to two times of rate constant (Fig. 13.2). This equation shows that value of C decreases with passage of time. It means reactants are consumed during polymerization.

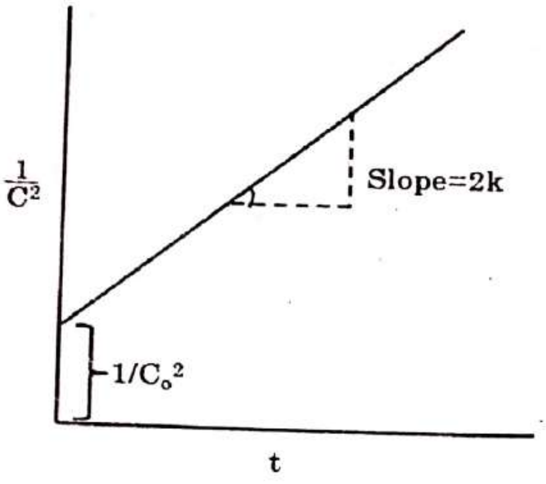


Fig. 13.2 Plot of $1/C^2$ versus time

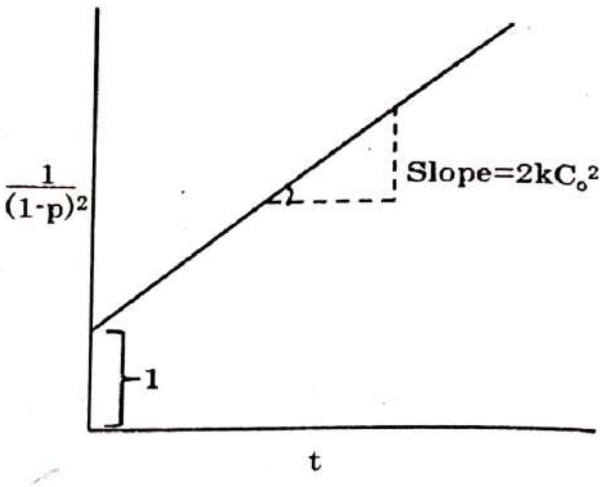


Fig. 13.3 Plot of $1/(1-p)^2$ versus time

It was assumed that concentration of water is negligible.

Extent of reaction (p) is stated as the fraction of functional groups that have consumed at time t. It is ratio of –COOH groups reacted to initial concentration of –COOH [equation (13.8)]. As it is more convenient to express rate equation in terms of extent of reaction, thus relationship for extent of reaction and concentration is

$$p = \frac{C_o - C}{C_o} \tag{13.8}$$

$$pC_o = C_o - C$$

$$C = C_o - pC_o$$

$$C = C_o(1-p) \tag{13.9}$$

Putting value of C from equation (13.9) into (13.7), we get

$$\frac{1}{(C_o(1-p))^2} = \frac{1}{C_o^2} + 2kt$$

$$\frac{1}{C_o^2(1-p)^2} - \frac{1}{C_o^2} = 2kt$$

$$\frac{1}{C_o^2}\left(\frac{1}{(1-p)^2} - 1\right) = 2kt$$

$$\frac{1}{(1-p)^2} - 1 = 2C_o^2kt$$

$$\frac{1}{(1-p)^2} = 2C_o^2kt + 1 \tag{13.10}$$

Equation (13.10) is required rate expression in terms of extent of reaction. Following are results which can be obtained from this equation.

(i) Order of reaction is equal to three in self catalyzed step growth polymerization.

(ii) Units of rate constant are $dm^6mol^{-2}s^{-1}$.

(iii) Half life period for the reaction is inversely proportional to the square of initial concentration of reactant i.e.

From equation (13.7), we get

$$\frac{2}{C_o^2} = \frac{1}{C_o^2} + kt_{1/2}$$

$$\frac{1}{C_o^2} = kt_{1/2}$$

$$t_{1/2} \propto \frac{1}{C_o^2}$$

(iv) Fig. 13.3 is obtained from equation (13.10) which is a straight line equation in intercept form.

(v) Intercept of graph in Fig. 13.3 is 1 while its slope is $2kC_o^2$. As C_o is known mostly, thus value of slope helps to find value of rate constant of reaction.

(vi) Maximum and ideal value of extent of reaction is 1. This equation helps to find time when extent of reaction becomes 1. As $p \rightarrow 1$, then $(1-p)^2 \sim 0$, applying these conditions to equation (13.10)

$$\frac{1}{(1-p)^2} = 2C_o^2kt + 1$$

$$\infty = 2C_o^2kt + 1$$

Ignoring value of intercept as it is very much small as compared to infinity.

Thus

$$\infty = 2C_o^2kt \qquad (13.11)$$

This equation shows that product of 2, k, t and C_o^2 is infinity. 2, k and C_o^2 are constants. Thus time is only variable. It means infinite time is required in step growth polymerization to achieve 100 % conversion of reactants into products.

(b) In the Presence of Acid Catalyst

Rate of consumption of –COOH is also equal to rate of consumption of –OH here and represents rate of reaction in the presence of acid catalyst.

$$\text{Rate of reaction} = -\frac{d[COOH]}{dt} = -\frac{d[OH]}{dt}$$

Rate of reaction between carboxylic acid and alcohol in the presence of any external acid catalyst is a second order reaction. Rate of reaction is directly proportional to first power of concentrations of alcohol, acid and catalyst. But concentration of catalyst remains constant during the progress of reaction. So,

$$\text{Rate of reaction} \propto [OH][COOH][H^+] \qquad (13.12)$$

Thus rate of reaction can be written in terms of rate of consumption of –OOH.

$$-\frac{d[COOH]}{dt} \propto [OH][COOH][H^+]$$

$$-\frac{d[COOH]}{dt} = k[OH][COOH][H^+] \qquad (13.13)$$

k is rate constant of acid catalyzed reaction.

Catalyst is that specie which does not consume during reaction and boosts up rate of reaction only. Thus concentration of H^+ remains constant throughout polymerization. So

$$k' = k[H^+] \qquad (13.14)$$

k' is another constant which is can be substituted instead of $k[H^+]$ in equation (13.13).

$$-\frac{d[COOH]}{dt} = k'[OH][COOH] \qquad (13.15)$$

Concentration of each of the monomers at any time is C. So

$$-\frac{dC}{dt} = k'C^2$$

$$-\frac{dC}{C^2} = k'dt \qquad (13.16)$$

Integrating above equation, we get

$$-\int\frac{dC}{C^2} = k'\int dt$$

$$-\left[\frac{C^{-2+1}}{-2+1}\right] = k't + c$$

$$\frac{1}{C} = k't + c \qquad (13.17)$$

C_o is initial concentration of acid, it means C_o is concentration of acid at time=0. Thus on application of boundary conditions, we get

$$c = \frac{1}{C_o}$$

Putting value of c from above equation into equation (13.17), we get

$$\frac{1}{C} = k't + \frac{1}{C_o} \qquad (13.18)$$

Equation (13.18) is rate equation for acid catalyzed step growth polyesterification. Following results are deduced from this equation.

(i) This is a straight line equation in intercept form.

(ii) Intercept of graph manipulated from equation (13.18) is equal to inverse of initial concentration of one of the monomers as sketched in Fig. 13.4.

(iii) Slope of plot of Fig. 13.3 is equal to constant k′ (Fig. 13.4).

On comparison of equation (13.18) and (13.13), we deduced that intercept is greater in the presence of external acid catalyst as compared to absence of external catalyst. We also inferred that slope is greater in case of acid catalyzed polymerization as compared to that of no external catalyst, because slope is ratio of $1/C^2$ to time in the absence of catalyst while it is ratio of 1/C to time in the absence of catalyst. Square of concentration in the absence of catalyst more rapidly decreases value of slope and hence value of rate constant of polymerization. Thus comparison of equations (13.13) and (13.18) verifies that rate of reaction is faster in the presence of catalyst rather in the absence of catalyst.

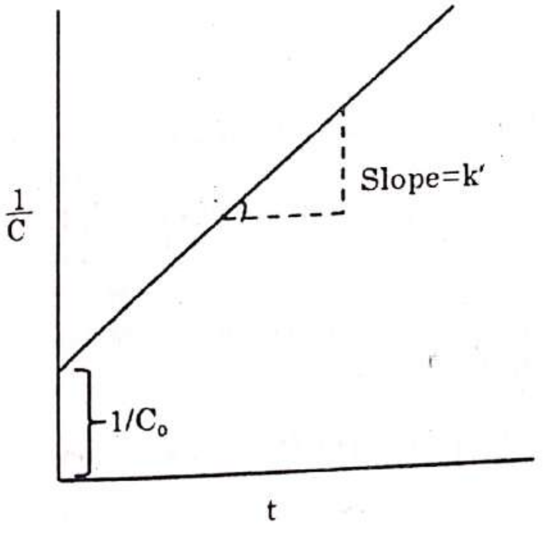


Fig. 13.4 Plot of 1/C versus time

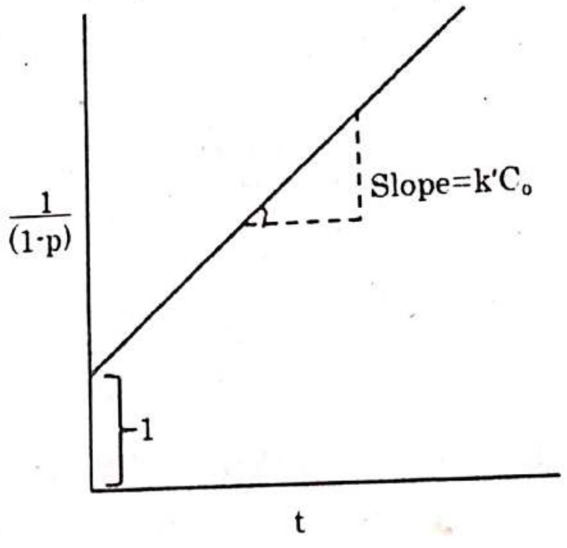


Fig. 13.5 Plot of 1/(1-p) versus time

It was assumed that concentration of water is negligible.

From equation (13.9), available concentration of reactant in terms of extent of reaction can be written as

$$C = C_o(1-p)$$

Putting value of C from above equation into (13.18), we get

$$\frac{1}{C_o(1-p)} = \frac{1}{C_o} + k't$$

$$\frac{1}{C}\left(\frac{1}{(1-p)}-1\right)=k't$$

$$\frac{1}{(1-p)}-1=Ck't$$

$$\frac{1}{(1-p)}=Ck't+1 \qquad (13.19)$$

Equation (13.19) is required rate expression in terms of extent of reaction. Following are results which can be obtained from this equation.

(iv) Fig. 13.5 is obtained from equation (13.19) which is a straight line equation in intercept form.

(v) Intercept of graph in Fig. 13.5 is 1 while its slope is $k'C_o$. As C_o is known mostly, thus value of slope helps to find value of rate constant of reaction.

(vi) This equation also helps to find time when extent of reaction becomes 1. As $p\rightarrow1$, then $(1\text{-}p) \sim 0$, applying these conditions to equation (13.19)

$$\infty = C_o k't+1$$

Ignoring value of intercept as it is very much small as compared to infinity. Thus

$$\infty = C_o k't$$

This equation shows that product of k′, t and C_o is infinity. k′ and C_o are constants. Similar to polymerization in the absence of external catalyst, here infinite time is also required in acid catalyzed step growth polymerization to achieve 100 % conversion of reactants into products. It means 100 % conversion cannot be achieved even with use of catalyst. However, that polymer which is commercially synthesized in larger period of time will be synthesized in shorter time with use of catalyst.

13.4.3 Molecular Weight of Polymer in Step Growth Polymerization

Number average molecular weight (M_n) of polymer is equal to product of molecular weight of repeating unit of polymer (m) and number average degree of polymerization ($\overline{x_n}$). So

$$M_n = m \times \overline{x}_n \qquad (13.20)$$

$\overline{x}_n$ is equal to ratio of total number of molecules of succinic acid initially (N_o) to number of molecules of acid present in reaction at time t, so

$$\overline{x}_n = \frac{N_o}{N} \qquad (13.21)$$

Extent of reaction in terms of number of molecules is

$$p = \frac{N_o - N}{N_o}$$

$$pN_o = N_o - N$$

$$N = N_o - pN_o$$

$$N = N_o(1-p)$$

$$\frac{N_o}{N} = \frac{1}{(1-p)} \qquad (13.22)$$

By equating equations (13.22) and (13.21), we get Carother's equation (13.23).

$$\overline{x}_n = \frac{1}{(1-p)} \qquad (13.23)$$

When $p \to 1$ then $\overline{x}_n \to \infty$, it shows that high $\overline{x}_n$ can be obtained at high degree of conversion.

Comparing equation (13.20) and (13.23)

$$M_n = m \times \frac{1}{(1-p)}$$

With the help of above equation, we deduced when $p \to 1$ then $M_n \to \infty$. It shows that high M_n can be obtained at high degree of conversion.

$$(1-p) = \frac{m}{M_n} \qquad (13.24)$$

(c) In the Absence of Acid Catalyst

For M_n of step growth polymer synthesized in the absence of catalyst, put value of (1-p) from equation (13.24) into equation (13.10) to get

$$\left(\frac{M_n}{m}\right)^2 = 2kC_o^2t + 1 \qquad (13.25)$$

Equation 13.25 says that $\left(\frac{M_n}{m}\right)^2$ is a linear function of time. It means M_n increases with passage of time. For infinite value of times, M_n will be very high.

(d) In the Presence of Acid Catalyst

For M_n of step growth polymer synthesized in the presence of catalyst, put value of (1-p) from equation (13.24) into equation (13.19)

$$\frac{M_n}{m} = Ck't + 1 \qquad (13.26)$$

It is inferred from equation (13.26) that M_n is almost directly proportional to t. It means M_n increases with passage of time.

Example 13.2

Tetramethylenediamine and succinic acid with 1:1 mole ratio react with each other to form a polymer. Calculate the number average degree of polymerization for 3% conversion of each reactant into polymer.

Solution

Number of unreacted specie=N=3

Total amount of species participate in reaction=N_o=97

Degree of polymerization=$\bar{x}_n$=?

As we know that

$$P = \frac{N_o - N}{N_o}$$

By putting values, we get

$$P = \frac{100-3}{100}$$

$$P = 0.97$$

By using Carothers's equation

$$\bar{x}_n = \frac{1}{(1-p)}$$

By putting value of P in above equation we get

$$\bar{x}_n = \frac{1}{(1-0.97)}$$

$$\bar{x}_n = 16.92$$

Example 13.3

Calculate the number average degree of polymerization for a monomer conversion of 98%and 99% using Carothers's equation for the reaction of one mole of adipic acid with one mole of hexamethylenediamine to produce Nylon-6, 6.

Solution

(i) $N_0 = 100$

$N = 2$

As we know that

$$P = \frac{N_0 - N}{N_0}$$

By putting values in above equation, we get

$$P = \frac{100-2}{100}$$

$$P = 0.98$$

By using Carothers's equation

$$\bar{x}_n = \frac{1}{(1-p)}$$

By putting value of P in above equation, we get

$$\bar{x}_n = \frac{1}{(1-0.98)}$$

$$\bar{x}_n = 50$$

(ii) $N_0 = 100$

$N = 1$

As we know that

$$P = \frac{N_0 - N}{N_0}$$

$$P = \frac{100-1}{100}$$

$$P = 0.99$$

By using Carothers's equation

$$\bar{x}_n = \frac{1}{(1-p)}$$

By putting value of P in above equation, we get

$$\bar{x}_n = \frac{1}{(1-0.99)}$$

$$\bar{x}_n = 100$$

13.5 CHAIN GROWTH POLYMERIZATION

Chain growth polymerization occurs through a reactive centre or carrier specie. Carrier specie grows by combining with monomers and polymerization occurs.

13.5.1 Types of Chain Growth Polymerization

There are four basic types of chain growth polymerization on the basis of nature of chain carrier specie. Free radical, cation, anion and co-ordination polymerizations are these four types, if chain carrier species are free radical, cation, anion and specie having properties of charge as well as free radical respectively.

13.5.2 Steps of Chain Growth Polymerization

Initiation, propagation and termination are three basic steps of all types of chain polymerization.

(i) Initiation

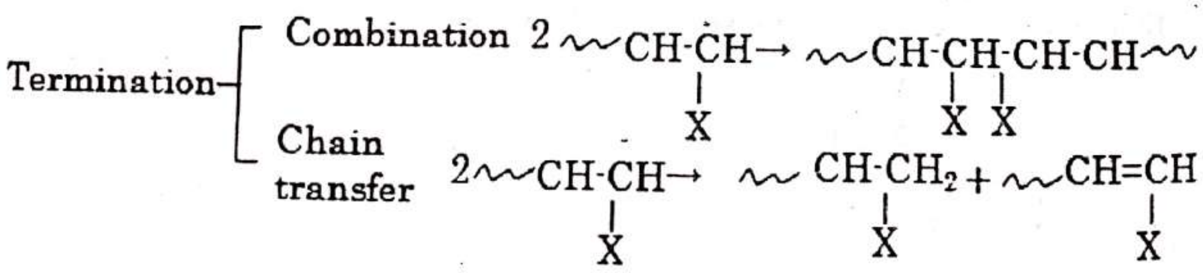
In initiation, initiator is added to generate a carrier specie which can be a radical or ion or have characteristics of radical along with that of ion. Sometimes initiator is not added, light rays or heat is used to break bonds in initiator and generates reactive centers. Bonds in initiator are weak, they easily break away and reactive centers are formed. These reactive centers react with monomer and transfer reactive center to monomer.

(ii) Propagation

During this process, low molecular weight species formed in initiation rapidly combine with more monomers and a high molecular weight polymer is synthesized. Thus this step can be called a growth step.

(iii) Termination

All reactive centers become inactive during this step. Combination (coupling) and chain transfer (disproportionation) are two routes of termination. During coupling two active polymer chains combine with each other and form a single polymer. Thus molecular weight of resulting polymer will be sum of two growing chains. On other side, disproportionation is little different from combination. Two growing polymer chains are also involved here but some atoms transfer from one chain to other. So that one chain develops double bond at one end and other chain only satisfies its active center. Suppose we have free radical polymerization, then termination by combination and chain transfer will be



$$\text{Termination}\begin{cases}\text{Combination} & 2\sim CH\text{-}\underset{X}{\dot{C}H} \rightarrow \sim CH\text{-}\underset{X}{CH}\text{-}\underset{X}{CH}\text{-}CH\sim \\ \text{Chain transfer} & 2\sim CH\text{-}\underset{X}{\dot{C}H} \rightarrow \sim \underset{X}{CH}\text{-}CH_2 + \sim CH{=}\underset{X}{CH}\end{cases}$$

13.5.3 Free Radical Chain Growth Polymerization

That type of chain growth polymerization in which carrier specie is a free radical called as free radical chain growth polymerization. This polymerization also has three steps: initiation, propagation and termination.

(i) Initiation

During initiation, initiator (I) dissociates and produces two primary free radicals represented by $\dot{R}$. Rate constant of initiator dissociation is k_d. Then $\dot{R}$ reacts with monomer M and produces $\dot{M}_1$. Rate constant of this reaction is k_i. Specie $\dot{M}_1$ is basically $R-\dot{M}$, so $\dot{M}_1$ has R as neutral end group on one side and M as free radical end group on other side. Thus R itself becomes neutral by developing bond with M and converts M to a free radical. $\dot{M}_1$ is birth mark of polymer chain.

$$I \xrightarrow{k_d} 2\dot{R} \qquad (13.27)$$

$$\dot{R} + M \xrightarrow{k_i} \dot{M}_1 \qquad (13.28)$$

Among these two reactions of initiation, reaction represented in equation (13.27) is slow while other reaction is fast. This is solely due to the high reactivity of free radicals. Thus dissociation of initiator is rate determining step of initiation.

Initiator forms free radicals ($\dot{R}$) in pairs, so there are chances that these free radicals neutralize each other due to cage effect of solvent. As free radicals are present in cage of solvent molecules which does not let free radicals to move apart easily. So there are chances to recombination of $\dot{R}$. Thus fraction of generated free radicals gets wasted. Chances of recombination of $\dot{R}$ are much high under usage of high concentration of I.

Moreover $\dot{R}$ can also react with oxygen, thus presence of oxygen is also a cause behind wastage of primary radicals. Primary radicals also consumed during termination. Some radicals join with growing chain ($\dot{M}_y$) and produces dead polymer ($R-M_y$).

$$\dot{R} + \dot{M}_y \xrightarrow{\text{Termination}} R-M_y$$

Thus a number of routes are possible by which initiator efficiency (f) gets reduced, as ratio of number of polymerization initiating radicals to total number of generated primary radicals is initiator efficiency.

(ii) Propagation

Propagation is second and fast step in which monomers are rapidly added to a growing chain and high molecular weight chain is formed. $\dot{M}_1$ reacts with M and forms $\dot{M}_2$. Similarly $\dot{M}_2$ reacts and form a long polymer chain. It is assumed that rate of propagation does not depends upon length of polymer chain, so almost all monomers have consumed during propagation, thus rate of propagation is considered equal to rate of polymerization.

$$\dot{M}_1 + M \xrightarrow{k_p} \dot{M}_2$$

$$\dot{M}_2 + M \xrightarrow{k_p} \dot{M}_3 \qquad (13.29)$$

$$\dot{M}_n + M \xrightarrow{k_p} \dot{M}_{n+1}$$

(iii) Termination

Growth of chains stops in this step. Growing polymer chains also stabilize them in this step by disproportionation and combination processes.

Following are some characteristics of combination process.

(a) It is a bimolecular process as two growing chains are involved in it.

(b) Combination results in a polymer of greater molecular weight as compared to weight of individual growing chains.

(c) Total number of dead polymer chains produced by combination is half as compared to that of growing chains which combined to form dead polymer.

(d) Polymers formed by combination have two initiator primary radicals per molecule of polymer, as initiator radicals are present at both ends of chain as end group. By determining number of end groups in a chain we can manipulate that this polymer is terminated by combination or not.

(e) $\dot{M}_n$ and $\dot{M}_m$ are two growing chains, they combine and form a dead polymer M_{n+m}. Bond between $\dot{M}_n$ and $\dot{M}_m$ in M_{n+m} just like this $M_n - M_m$. In this high molecular weight polymer is formed by combination as compared to that by disproportionation.

$$\dot{M}_n + \dot{M}_m \xrightarrow{k_{tc}} M_{n+m} \tag{13.30}$$

Following are some characteristics of disproportionation process.

(a) Disproportionation is also a bimolecular process.

(b) Number of dead polymers formed by disproportionation is equal to number of reactant growing chains.

(c) Out of two terminated dead polymers, one has unsaturation and other has not.

(d) Dead polymers produced by disproportionation have one primary free radical per dead polymer. Primary radical is present only at one end of dead polymer as end group while monomer is present at other end of polymer.

(e) M'_n and M'_m are two dead polymers formed from $\dot{M}_n$ and $\dot{M}_m$ terminated by disproportionation process. Some atoms are transferred from $\dot{M}_m$ to $\dot{M}_n$ and saturated M'_n and unsaturated M'_m produced. Thus by determination of unsaturation similar to monomer in end group of polymer, it can be deduced that the polymer is terminated by disproportionation.

$$\dot{M}_n + \dot{M}_m \xrightarrow{k_{td}} M'_n + M'_m \tag{13.31}$$

13.5.3.1 Kinetics of Free Radical Chain Growth Polymerization

Kinetic study of chain growth polymerization is manipulated from kinetic study of all three steps: initiation, propagation and termination. of chain polymerization.

(a) Initiation

As rate determining step is dissociation of initiator because $k_d <<< k_i$, so we have to consider equation (13.27) for determination of rate of initiation (R_i). R_i is equal to rate of formation of $\dot{M}_1$.

$$R_i = \frac{d[\dot{M}_1]}{dt} \tag{13.32}$$

Rate of decomposition of initiator is equal to half of rate of formation of $\dot{M}_1$, because one molecule of initiator produces two molecules of primary radicals and two $\dot{R}$ can produce two molecules of $\dot{M}_1$. So

$$-\frac{d[I]}{dt} = \frac{1}{2}\frac{d[\dot{M}_1]}{dt} \tag{13.33}$$

From equation (13.27), we get

$$-\frac{d[I]}{dt} = k_d[I] \tag{13.34}$$

Equating equation (13.33) and (13.34)

$$\frac{1}{2}\frac{d[\dot{M}_1]}{dt} = k_d[I]$$

$$\frac{d[\dot{M}_1]}{dt} = 2k_d[I] \tag{13.35}$$

Thus R_i is

$$R_i = 2k_d[I]$$

As previously explained that all generated initiator molecules do not involved in initiation of polymerization. A number of molecules get wasted by oxygen gas, solvent cage effect and due to many other reasons. Therefore only a fraction (f) is involved in initiation of polymerization, so above equation will be

$$R_i = \frac{d[\dot{M}]}{dt} = 2fk_d[I] \tag{13.36}$$

(b) Propagation

Rate of propagation is equal to rate of consumption of monomer M. Thus using reactions of equation (13.29), rate of propagation is generally written as

$$R_p = -\frac{d[M]}{dt} = k_p[\dot{M}][M] \tag{13.37}$$

(c) Termination

Equations (13.30) and (13.31), both shows chain termination is a bimolecular process whether occurs by combination or chain transfer. So rate of termination is deduced as

$$R_{tc} = k_{tc}\left[\dot{M}\right]\left[\dot{M}\right] \quad \text{(termination by combination)} \qquad (13.38)$$

$$R_{td} = k_{td}\left[\dot{M}\right]\left[\dot{M}\right] \quad \text{(termination by disproportionation)} \quad (13.39)$$

Adding equation (13.39) and (13.38) as termination occurs by both routes

$$R_t = R_{tc} + R_{td}$$

$$R_t = k_{tc}\left[\dot{M}\right]\left[\dot{M}\right] + k_{td}\left[\dot{M}\right]\left[\dot{M}\right]$$

$$R_t = (k_{tc} + k_{td})\left[\dot{M}\right]^2$$

$$R_t = k_t\left[\dot{M}\right]^2 \qquad (13.39a)$$

And rate of consumption of $\dot{M}$ during termination is

$$R_t = -\frac{1}{2}\frac{d\left[\dot{M}\right]}{dt} = k_t\left[\dot{M}\right]^2$$

$$-\frac{d\left[\dot{M}\right]}{dt} = 2k_t\left[\dot{M}\right]^2 \qquad (13.40)$$

Practically quantity of $\dot{M}$ is negligible. it means rate of formation of $\dot{M}$ during initiation is equal to rate of consumption of $\dot{M}$ during termination. So on application of steady state condition

$$-\frac{d\left[\dot{M}\right]}{dt} = 0$$

$$+\frac{d\left[\dot{M}\right]}{dt} = -\frac{d\left[\dot{M}\right]}{dt} \qquad (13.41)$$

Putting values from equations (13.36) and (13.40) respectively into equation (13.41)

$$2fk_d[I] = 2k_t\left[\dot{M}\right]^2 \qquad (13.41a)$$

$$\left[\dot{M}\right]^2 = \frac{fk_d[I]}{k_t} \qquad (13.41b)$$

Taking square root of above equation

$$\sqrt{[\dot{M}]^2} = \sqrt{\frac{fk_d[I]}{k_t}}$$

$$[\dot{M}] = \sqrt{\frac{fk_d[I]}{k_t}} \qquad (13.42)$$

Substituting value of $[\dot{M}]$ from equation (13.42) into equation (13.37)

$$R_p = k_p[M]\sqrt{\frac{fk_d[I]}{k_t}}$$

$$R_p = k_p[M]\left(\frac{fk_d[I]}{k_t}\right)^{\frac{1}{2}} \qquad (13.43)$$

Following are results drawn from equation (13.43)

(i) Equation (13.43) is a straight line equation passing through origin.

(ii) k_p, k_d, k_t and f are constants. If we kept [M] constant, then rate of polymerization directly depends upon square root of concentration of initiator as shown in Fig. 13.6.

$$R_p \propto [I]^{\frac{1}{2}} \qquad \text{(when [M] is constant)}$$

(iii) Similarly if we kept $[I]^{1/2}$ constant, then rate of polymerization is directly proportional to concentration of monomer as shown in Fig. 13.7.

$$R_p \propto [M] \text{ (when } [I]^{1/2} \text{ is constant)}$$

(iv) Comparison of points (ii) and (iii) shows that R_p more significantly depends upon concentration of monomer, as R_p is proportional to square root of [I] and first power of [M].

(v) If efficiency of utilization of primary free radical does not depend upon concentration of monomer, then f will be considered constant and

$$\frac{R_p}{[M][I]^{\frac{1}{2}}} = k_p\left(\frac{fk_d}{k_t}\right)^{\frac{1}{2}} = \text{constant}$$

Under this condition, by increasing concentration of monomer or initiator, rate of polymerization increases as ratio $R_p/[M][I]^{1/2}$ is a constant quantity.

Putting value of $[\dot{M}]$ into equation (13.39), expression for rate of termination can be deduced as

$$R_t = k_t\left(\frac{2fk_d[I]}{k_t}\right)$$

$$R_t = 2fk_d[I] \qquad (13.44)$$

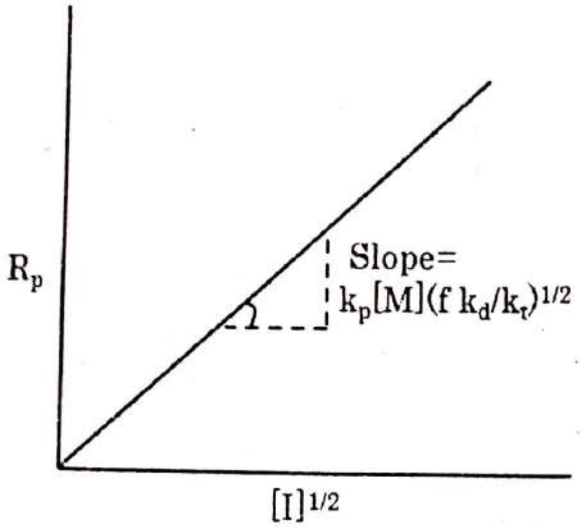


Fig. 13.6 Plot of R_p versus $[I]^{1/2}$.

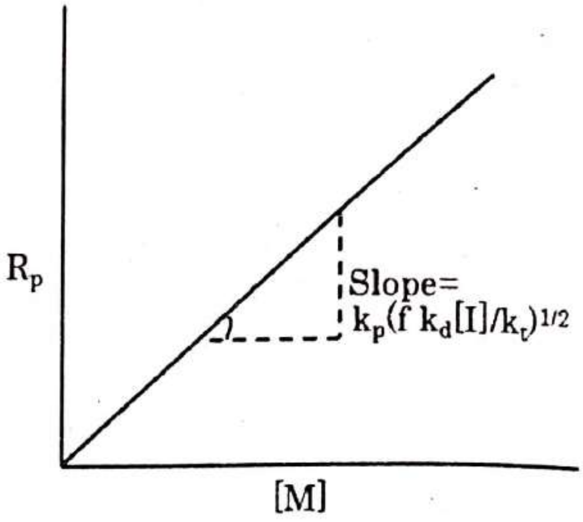


Fig. 13.7 Plot of R_p versus [M].

Results drawn from equation (13.44) are

(i) Equation (13.44) is a straight line equation passing through origin.

(ii) It is deduced from this equation that R_t is linearly and positively dependent upon concentration of initiator as shown in Fig. 13.8. It means by increasing concentration of monomer, rate of termination increases.

$$R_t \propto [I]$$

(iii) Slope of this plot is equal to $2fk_d$. So by calculating slope, we can calculate rate of dissociation of initiator and can manipulate speed of initiation step.

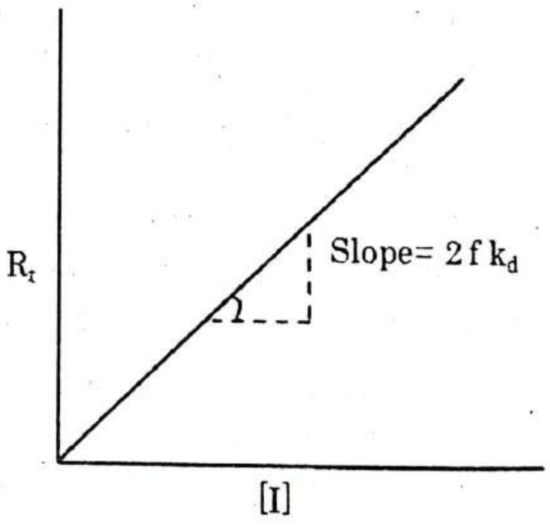


Fig. 13.8 Plot of R_t versus [I]

In this way, expressions for rate of propagation (13.43) and rate of termination (13.44) are derived which help to calculate rates along with concentration of initiator.

13.5.3.2 Degree of Polymerization

Number average degree of polymerization ($\bar{x}_n$) is ratio of rate of propagation and rate of termination. So

$$\bar{x}_n = \frac{\text{Rate of propagation}}{\text{Rate of termination}}$$

$$\bar{x}_n = \frac{R_p}{R_t} \qquad (13.45)$$

Putting values of R_p and R_t from equations (13.43) and (13.44)

$$\bar{x}_n = \frac{k_p[M]\left(\frac{fk_d[I]}{k_t}\right)^{\frac{1}{2}}}{2fk_d[I]}$$

$$\bar{x}_n = \frac{k_p\left(\frac{fk_d}{k_t}\right)^{\frac{1}{2}}[M][I]^{\frac{1}{2}}}{2fk_d[I]}$$

$$\bar{x}_n = \frac{k_p\left(\frac{1}{k_t}\right)^{\frac{1}{2}}[M]}{2(fk_d)^{\frac{1}{2}}[I]^{\frac{1}{2}}}$$

$$\bar{x}_n = \frac{k_p[M]}{2(fk_tk_d)^{\frac{1}{2}}[I]^{\frac{1}{2}}} \qquad (13.46)$$

Equation (13.46) helps to conclude following results

(i) Equation (13.46) is a straight line equation passing through origin.

(ii) $\bar{x}_n$ is directly proportional to concentration of monomer, means high concentration of monomer helps to build polymer of long length.

(iii) $\bar{x}_n$ is inversely proportional to square root of concentration of initiator which is contrary to equation (13.43), where rate of polymerization is directly proportional to square root of concentration of initiator. It means if we increase concentration of initiator, then rate of polymerization increases but chain length decreases. Rate of polymerization increases, because larger number of initiator molecules can generate large quantity of primary free radicals, which have ability to react with a greater quantity of monomers and speeds up polymerization rate. On the other hand, by employing high concentration of initiator, there are greater chances of growing polymer chains to combine with primary free radicals of initiator and terminates polymerization, thus chain length decreases. In this way, concentration of initiator has dual effect. If we gain in speed of polymerization, then we lose chain length at the same time.

13.5.3.4 Kinetic Chain Length

Number of monomer molecules that consumed by a single primary free radical which can initiates polymerization of a chain is called kinetic chain length. Kinetic chain length is directly proportional to $\bar{x}_n$.

$$\bar{x}_n \propto \nu$$

$$\bar{x}_n = (\text{constant})\,\nu \qquad (13.47)$$

Value of constant of above equation depends upon route of termination; combination or disproportionation, adopted by growing polymer chain.

(i) Combination

Value of constant is 2 for termination by combination, because in combination two polymer chains combine and $\bar{x}_n$ becomes double of kinetic chain length. Thus equation (13.47) will be

$$\bar{x}_n = 2\nu$$

$$\nu = \frac{\bar{x}_n}{2} \qquad (13.48)$$

Putting value of $\bar{x}_n$ from equation (13.46) into equation (13.48)

$$\nu = \frac{\dfrac{k_p[M]}{2(fk_t k_d)^{\frac{1}{2}}[I]^{\frac{1}{2}}}}{2}$$

$$\nu = \frac{1}{2}\left(\frac{k_p[M]}{2(fk_t k_d)^{\frac{1}{2}}[I]^{\frac{1}{2}}}\right)$$

$$\nu = \frac{k_p[M]}{4(fk_t k_d)^{\frac{1}{2}}[I]^{\frac{1}{2}}} \qquad (13.49)$$

Equation (13.49) shows similar results to equation (13.46). It also shows inverse relation with $[I]^{1/2}$ and direct with [M]. In addition to $\bar{x}_n$, kinetic chain length is another parameter to study length of polymer chains. So, similar results are drawn.

(ii) Disproprtionation

Value of constant is 1 for termination by disproportionation. It is because two polymer chains do not combine, some atoms are transferred from one chain to other only. Thus $\bar{x}_n$ becomes equal to kinetic chain length. Thus equation (13.47) will be

$$\bar{x}_n = \nu \qquad (13.50)$$

Putting value of $\bar{x}_n$ from equation (13.46) into equation (13.50)

$$\nu = \frac{k_p[M]}{2(fk_t k_d)^{\frac{1}{2}}[I]^{\frac{1}{2}}} \qquad (13.51)$$

Equation (13.51) shows similar results to equation (13.49) as equation (13.51) is similar to equation (13.49).

13.5.3.5 Instantaneous Kinetic Chain Length

Instantaneous kinetic chain length is ratio of rate of formation of growing polymer chains and rate of formation of dead polymers. Instantaneous kinetic chain length provides picture in terms of termination processes rather effective fraction off initiator primary radicals. So

$$\nu_i = \frac{\text{Rate of formation of growing polymer chains}}{\text{Rate of formation of dead polymer chains}} \qquad (13.52)$$

If all dead polymer chains are represented by Y, then

$$2\dot{M} \xrightarrow{k_{tc}} Y \quad \text{(combination)}$$

Rate of termination by combination (R_{tc}) is given as

$$R_{tc} = +\frac{d[Y]}{dt} = k_{tc}[\dot{M}]^2 \qquad (13.53)$$

and

$$2\dot{M} \xrightarrow{k_{td}} 2Y \quad \text{(disproportionation)}$$

Rate of termination by disproportionation (R_{td}) is given as

$$R_{td} = +\frac{1}{2}\frac{d[Y]}{dt} = k_{tc}[\dot{M}]^2$$

$$+\frac{d[Y]}{dt} = 2k_{td}[\dot{M}]^2 \qquad (13.54)$$

Overall rate of formation of dead chains during termination is obtained by adding equation (13.53) and (13.54)

$$+\frac{d[Y]}{dt} = k_{tc}[\dot{M}]^2 + 2k_{td}[\dot{M}]^2$$

$$\frac{d[Y]}{dt} = (k_{tc} + 2k_{td})[\dot{M}]^2 \qquad (13.55)$$

Putting values of rate of formation of growing radicals and rate of formation of dead chains from equation (13.37) and (13.55) respectively into equation (13.52)

$$\nu_i = \frac{k_p[M][\dot{M}]}{(k_{tc} + 2k_{td})[\dot{M}]^2}$$

$$\nu_i = \frac{k_p[M]}{(k_{tc} + 2k_{td})[\dot{M}]} \qquad (13.56)$$

For more detailed and comprehensive view, a new parameter ξ introduced. ξ is used to express rate of formation of dead polymer chains per termination. So that it can be manipulated that whether combination or disproportionation, process of termination is contributing more in termination. So

$$\xi = \frac{\text{Rate of formation of dead chains}}{\text{Rate of termination}}$$

Putting value from equation (13.55) into above equation

$$\xi = \frac{(k_{tc} + 2k_{td})[\dot{M}]^2}{k_t[\dot{M}]^2}$$

$$\xi = \frac{k_{tc} + 2k_{td}}{k_t} \qquad (13.57)$$

Thus v_i and ξ provides a better study. Equation (13.57) shows that it is a constant factor which is independent of concentration of monomer and initiator, while equation (13.56) shows that v_i positively depends upon concentration of monomer.

13.5.3.6 Chain Transfer

When a growing polymer chain becomes dead polymer and a new one is initiated, this is termed as chain transfer. Transfer agent in chain transfer is not monomer only, but it can occur with solvent, initiator, polymer and modifier. Let we have a growing polymer chain ($\dot{M}_n$) and transfer agent XY, both reacts and form stable $M_n - X$ and free radical $\dot{Y}$.

$$\dot{M}_n + XY \rightarrow M_n - X + \dot{Y}$$

(i) Monomer Transfer

When a growing polymer chain ($\dot{M}_n$) converts a monomer into a free radical and itself become stable, then monomer transfer occurs.

$$\dot{M}_n + M \xrightarrow{k_{tr.M}} M_n + \dot{M}$$

Rate of monomer transfer can be written by using above reaction

$$R_{tr.M} = k_{tr.M}[\dot{M}_n][M] \qquad (13.58)$$

Where $k_{tr.M}$ is rate constant of monomer transfer reaction. Transfer constant of monomer transfer is

$$C_{tr.M} = \frac{k_{tr.M}}{k_p} \qquad (13.59)$$

(ii) Solvent Transfer

Solvent transfer occurs when growing polymer chain ($\dot{M}_n$) is involved with solvent molecules (S). As result of chain transfer, solvent molecules convert into free radicals and polymer chain becomes stable.

$$\dot{M}_n + S \xrightarrow{k_{tr,S}} M_n + \dot{S}$$

Rate of solvent transfer can be written by using above reaction

$$R_{tr,S} = k_{tr,S}\left[\dot{M}_n\right][S] \quad (13.60)$$

Where $k_{tr,S}$ is rate constant of solvent transfer reaction. Solvent transfer constant is

$$C_{tr,S} = \frac{k_{tr,S}}{k_p} \quad (13.61)$$

(ii) Initiator Transfer

Chain transfer agent is initiator in initiator transfer. Here is its chain transfer reaction

$$\dot{M}_n + I \xrightarrow{k_{tr,I}} M_n + \dot{I}$$

Rate of initiator transfer is

$$R_{tr,I} = k_{tr,I}\left[\dot{M}_n\right][I] \quad (13.62)$$

Where $k_{tr,I}$ is rate constant of initiator transfer reaction. Initiator transfer constant can be written as

$$C_{tr,I} = \frac{k_{tr,I}}{k_p} \quad (13.63)$$

As we know number average degree of polymerization ($\bar{x}_n$) is ratio of propagation rate and termination rate. But here many chain transfer reactions are possible, so $\bar{x}_n$ is ratio of propagation rate to sum of termination rates by all processes.

$$\bar{x}_n = \frac{\text{Rate of chain growth}}{\text{Sum of rate of formation of dead polymers by all processes}}$$

In addition to monomer transfer, solvent transfer and initiator transfer, termination is also included in dead polymer formation. Thus above equation will be

$$\bar{x}_n = \frac{R_p}{R_{tr,M} + R_{tr,S} + R_{tr,I} + R_t}$$

$$\frac{1}{\bar{x}_n} = \frac{R_{tr,M} + R_{tr,S} + R_{tr,I} + R_t}{R_p} \quad (13.64)$$

Putting value of R_t from equation (13.39a) into (13.41a)

$$2fk_d[I] = 2R_t$$

$$R_t = fk_d[I] \tag{13.65}$$

Putting values of $R_{tr.M}$, $R_{tr.S}$, $R_{tr.I}$, R_p and R_t from equations (13.58), (13.60), (13.62), (13.37) and (13.65) into (13.64)

$$\frac{1}{x_n} = \frac{k_{tr.M}[\dot{M}_n][M] + k_{tr.S}[\dot{M}_n][S] + k_{tr.I}[\dot{M}_n][I] + \left(\frac{2fk_d[I]}{2}\right)}{k_p[\dot{M}_n][M]}$$

$$\frac{1}{x_n} = \frac{k_{tr.M}[\dot{M}_n][M] + k_{tr.S}[\dot{M}_n][S] + k_{tr.I}[\dot{M}_n][I] + fk_d[I]}{k_p[\dot{M}_n][M]}$$

$$\frac{1}{x_n} = \frac{k_{tr.M}[\dot{M}_n][M]}{k_p[\dot{M}_n][M]} + \frac{k_{tr.S}[\dot{M}_n][S]}{k_p[\dot{M}_n][M]} + \frac{k_{tr.I}[\dot{M}_n][I]}{k_p[\dot{M}_n][M]} + \frac{fk_d[I]}{k_p[\dot{M}_n][M]}$$

$$\frac{1}{x_n} = \frac{k_{tr.M}}{k_p} + \frac{k_{tr.S}[S]}{k_p[M]} + \frac{k_{tr.I}[I]}{k_p[M]} + \frac{fk_d[I]}{k_p[\dot{M}_n][M]} \tag{13.66}$$

Substituting $C_{tr.M}$, $C_{tr.S}$ and $C_{tr.I}$ into equation (13.66) by using equations (13.59), (13.61) and (13.63) respectively

$$\frac{1}{x_n} = C_{tr.M} + C_{tr.S}\frac{[S]}{[M]} + C_{tr.I}\frac{[I]}{[M]} + \frac{fk_d[I]}{k_p[\dot{M}_n][M]} \tag{13.67}$$

Using equation (13.41a), concentration of initiator is determined as

$$[I] = \frac{k_t[\dot{M}_n]^2}{fk_d} \tag{13.68}$$

Putting value of [I] from equation (13.68) into equation (13.67)

$$\frac{1}{x_n} = C_{tr.M} + C_{tr.S}\frac{[S]}{[M]} + C_{tr.I}\frac{1}{[M]}\left(\frac{k_t[\dot{M}_n]^2}{fk_d}\right) + \frac{fk_d}{k_p[\dot{M}_n][M]}\left(\frac{k_t[\dot{M}_n]^2}{fk_d}\right)$$

$$\frac{1}{x_n} = C_{tr.M} + C_{tr.S}\frac{[S]}{[M]} + C_{tr.I}\frac{k_t[\dot{M}_n]^2}{fk_d[M]} + \frac{k_t[\dot{M}_n]}{k_p[M]} \tag{13.69}$$

From equation (13.37), we get

$$[\dot{M}_n] = \frac{R_p}{k_p[M]}$$

Substituting value of $\left[\dot{M}_n\right]$ from above equation into equation (13.69)

$$\frac{1}{\bar{x}_n} = C_{tr,M} + C_{tr,S}\frac{[S]}{[M]} + C_{tr,I}\frac{k_t\left(\frac{R_p}{k_p[M]}\right)^2}{fk_d[M]} + \frac{k_t\left(\frac{R_p}{k_p[M]}\right)}{k_p[M]}$$

$$\frac{1}{\bar{x}_n} = C_{tr,M} + C_{tr,S}\frac{[S]}{[M]} + C_{tr,I}\frac{k_tR_p^2}{fk_dk_p^2[M][M]^2} + \frac{k_tR_p}{k_pk_p[M][M]}$$

$$\frac{1}{\bar{x}_n} = C_{tr,M} + C_{tr,S}\frac{[S]}{[M]} + C_{tr,I}\frac{k_tR_p^2}{fk_dk_p^2[M]^3} + \frac{k_tR_p}{k_p^2[M]^2}$$

or

$$\frac{1}{\bar{x}_n} = C_{tr,M} + C_{tr,S}\frac{[S]}{[M]} + C_{tr,I}\left(\frac{k_t}{fk_dk_p^2}\right)\frac{R_p^2}{[M]^3} + \left(\frac{k_t}{k_p^2}\right)\frac{R_p}{[M]^2} \quad (13.70)$$

Equation (13.70) gives average degree of polymerization in terms of chain transfer constants.

(iii) Chain Transfer to Solvent

If initiator of low $C_{tr,I}$ value is used and $R_p/[M]^2$ kept constant by adjusting the concentration of initiator, then equation (13.70) will be

$$\frac{1}{\bar{x}_n} = \frac{1}{\left(\bar{x}_n\right)_o} + C_{tr,S}\frac{[S]}{[M]} \quad (13.71)$$

Following results are drawn from equation (13.71)

(i) Equation (13.71) is a straight line equation in intercept form as shown in Fig. 13.9.

(ii) Slope of graph is equal to $C_{tr,S}$.

(iii) Intercept of the graph provides value of inverse of number average degree of polymerization in the absence of solvent transfer agent.

If [S]→0, then

$$\frac{1}{\bar{x}_n} = \frac{1}{\left(\bar{x}_n\right)_o}$$

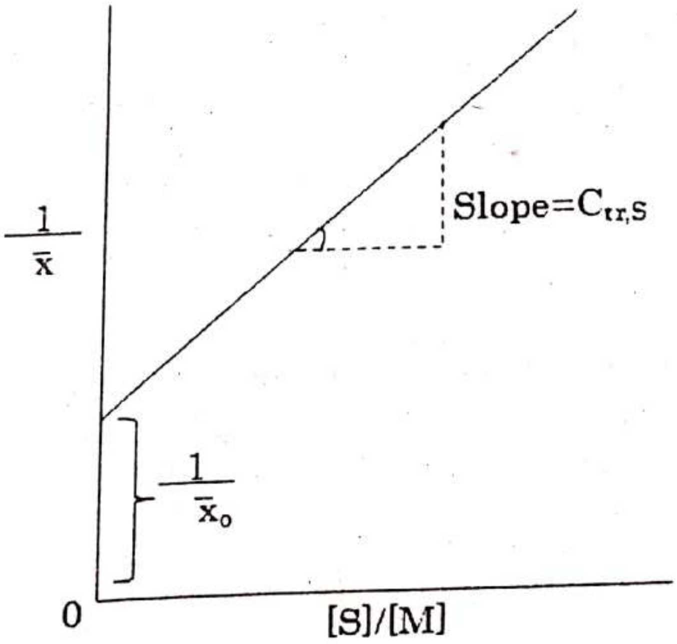


Fig. 13.9 Plot of [S]/[M] versus $\frac{1}{\bar{x}_n}$

Thus this graph provides values of constants, that is why it is excessively used to study free radical polymerization of styrene.

(iv) Chain Transfer to Monomer and Initiator

If chain transfer to solvent is absent, then equation (13.70) will be

$$\frac{1}{\overline{X}_n} = C_{tr,M} + C_{tr,I}\left(\frac{k_t}{fk_d k_p^2}\right)\frac{R_p^2}{[M]^3} + \left(\frac{k_t}{k_p^2}\right)\frac{R_p}{[M]^2}$$

Previous discussion shows that initial form of above equation is

$$\frac{1}{\overline{X}_n} = C_{tr,M} + C_{tr,I}\frac{[I]}{[M]} + \left(\frac{k_t}{k_p^2}\right)\frac{R_p}{[M]^2} \qquad (13.72)$$

Following results are drawn from equation (13.72)

(i) Equation (13.72) is a straight line equation in intercept form.

(ii) If R_p is plotted against $\frac{1}{\overline{X}_n}$, then for small values of [I], $[I] \to 0$, equation (13.72) will be

$$\frac{1}{\overline{X}_n} = C_{tr,M} + \left(\frac{k_t}{k_p^2}\right)\frac{R_p}{[M]^2}$$

As $C_{tr,M}$, k_t and k_p^2 are constants, so a linear plot obtained. Similar plot also obtained if $\frac{1}{\overline{X}_n}$ is plotted versus $1/[M]^2$.

(iii) For large values of [I], if R_p is plotted against $\frac{1}{\overline{X}_n}$ by using equation (13.72), then a non-linear graph results because role of chain transfer to initiator becomes prominent.

Thus this graph provides information about role of initiator on relation of R_p and $\frac{1}{\overline{X}_n}$ and, of $[M]^2$ and $\frac{1}{\overline{X}_n}$.

13.5.4 Mechanism and Kinetics of Cationic Chain Growth Polymerization

Typical catalysts for cationic polymerization are Lewis acids and Friedal Craft's catalysts such as $AlCl_3$, $AlBr_3$, BF_3, $SnCl_4$, H_2SO_4 and other acids. All these are strong electron acceptors. Most of them require co-catalyst to initiate copolymerization usually a base is used.

In this polymerization, the rate and average degree of polymerization can be given as

$$R_p = -\frac{d[M]}{dt} = k[Cat][M] \qquad (13.73)$$

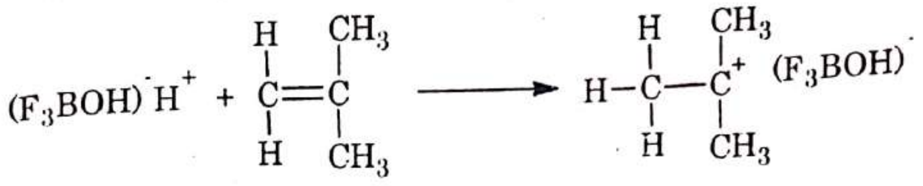
$$\overline{X}_n = k'[M]$$

These are the experimental results, to explain those facts we took the example of polymerization of isobutylene using BF_3 and H_2O as catalyst. The mechanism is consists of following steps

(i) **Initiation Process**

BF_3 and H_2O react to form a complex which adds a monomer unit to form a carbonium ion.

$$BF_3 + H_2O \rightarrow (F_3BOH)^-H^+ \quad \text{(complex catalyst)}$$

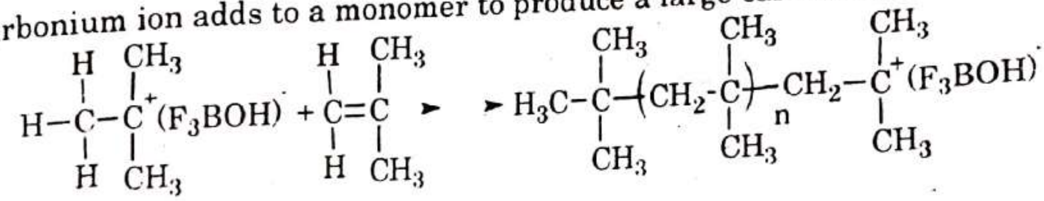


$$(F_3BOH)^-H^+ + \underset{H}{\overset{H}{C}}=\underset{CH_3}{\overset{CH_3}{C}} \longrightarrow H-\underset{H}{\overset{H}{C}}-\underset{CH_3}{\overset{CH_3}{C^+}}(F_3BOH)^-$$

Monomer Carbonium ion complex

(ii) **Propagation**

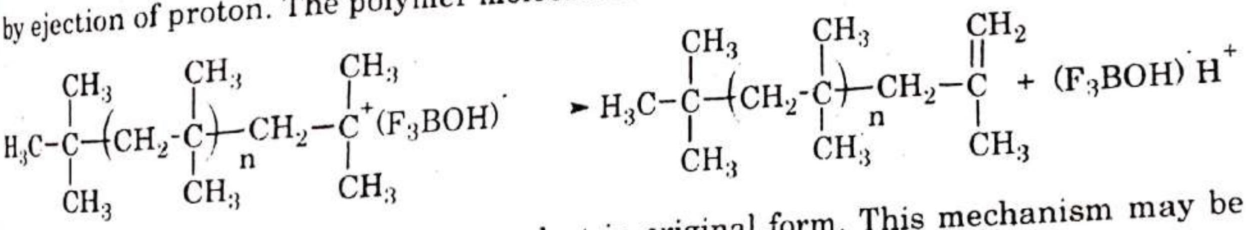
The carbonium ion adds to a monomer to produce a large carbonium ion.



$$H-\underset{H}{\overset{H}{C}}-\underset{CH_3}{\overset{CH_3}{C^+}}(F_3BOH)^- + \underset{H}{\overset{H}{C}}=\underset{CH_3}{\overset{CH_3}{C}} \rightarrow H_3C-\underset{CH_3}{\overset{CH_3}{C}}-\left(CH_2-\underset{CH_3}{\overset{CH_3}{C}}\right)_n-CH_2-\underset{CH_3}{\overset{CH_3}{C^+}}(F_3BOH)^-$$

(iii) **Termination**

In termination step, step active ion is deactivated to form a polymer molecule by ejection of proton. The polymer molecule has terminal unsaturation.



$$H_3C-\underset{CH_3}{\overset{CH_3}{C}}-\left(CH_2-\underset{CH_3}{\overset{CH_3}{C}}\right)_n-CH_2-\underset{CH_3}{\overset{CH_3}{C^+}}(F_3BOH)^- \rightarrow H_3C-\underset{CH_3}{\overset{CH_3}{C}}-\left(CH_2-\underset{CH_3}{\overset{CH_3}{C}}\right)_n-CH_2-\underset{CH_3}{\overset{CH_2}{\overset{\|}{C}}} + (F_3BOH)^-H^+$$

This step regenerates the catalyst in original form. This mechanism may be generalized as follows

Using A and BH for the catalyst and co-catalyst respectively, (AB) H^+ as the catalyst complex and $HMn^+(AB)$ as the carbonium ion complex. M as the monomer and M as the resulting polymer.

Initiation: $A + BH \rightarrow (AB)^- H^+$

Propagation: $HM_1^+(AB)^- + M_2 \rightarrow HM_2^+(AB)^-$

$$HM_2^+(AB)^- + M_n \rightarrow HM_n^+(AB)$$

Termination: $HM_n^+(AB)^- \rightarrow M_n + H^+(AB)^-$

The rates of individual steps are given below.

$$R_i = k_i[A] \qquad (13.74)$$

$$R_p = k_p[HM^+(AB)^-][M] \qquad (13.75)$$

$$R_t = k_t[HM^+(AB)^-] \qquad (13.76)$$

Since most of the monomer is consumed in the propagation step, one can assume that the rate of polymerization is given by equation (13.75). Since the concentration of carbonium ion complex $[HM^+(AB)\quad]$, the reaction intermediate, cannot be determined experimentally, the steady state approximation can be used to evaluate its concentration in terms of experimental quantities. Thus

$$R_i = R_t$$

$$k_i[A] = k_t[HM^+(AB)^-]$$

$$\frac{k_i}{k_t}[A] = [HM^+(AB)^-]$$

Putting this value in equation (13.75)

$$R_P = k_P\frac{k_i}{k_t}[A][M] \qquad (13.77)$$

Which is in good agreement with experimental equation (13.75) when

$$k = k_p\frac{k_i}{k_t}$$

The degree of polymerization is

$$\overline{X}_n = \frac{R_P}{R_t} = \frac{k_p[HM^+(AB)^-][M]}{k_t[HM^+(AB)^-]}$$

$$\overline{X}_n = \frac{k_p[M]}{k_t}$$

Which is in good agreement with experimental equation (13.76) when

$$k' = \frac{k_p}{k_t}$$

Therefore the proposed mechanism explains the experimental results. This mechanism is basic and simple.

Similarly styrene can be polymerized with trifluro acetic acid as catalyst.

13.5.5 Mechanism and Kinetics of Anionic Chain Growth Polymerization

Anionic polymerization involves the formation of anion. It occurs in the presence of a catalyst which yields electron readily, i.e. electron donors. For example triphenyl methyl sodium, potassium amide, butyl lithium in benzene, alkali metal amides etc. We consider the polymerization of styrene using potassium amine (KNH_2) in liquid ammonia as catalyst.

(i) **Initiation**

$$K + NH_3 \rightarrow K^+NH_2^-$$

$$K^+NH_2^- \xleftrightarrow{K_d} K^+ + NH_2^-$$

$$NH_2^-\ (\text{catalyst}) + M \xrightarrow{k_i} NH_2M^- \quad (\text{chain carrier})$$

(ii) **Propagation**

$$NH_2M_x^-\ (\text{complex}) + M \xrightarrow{k_p} NH_2M_{x+1}^-$$

(iii) **Termination**

$$NH_2M_x^- + NH_3 \xrightarrow{k_t} NH_2M_xH + NH_2^-$$

The rates of individual steps are given below.

$$R_i = Kk_i[Cat][M] \tag{13.78}$$

$$R_P = k_P[complex][M] \tag{13.79}$$

$$R_t = k_t[complex][NH_3] \tag{13.80}$$

Since most of the monomer is consumed in the propagation step, one can assume that the rate of polymerization is given by equation (13.79), rate of propagation is

$$-\frac{d[M]}{dt} = k_P[complex][M]$$

The steady state approximation can be used to evaluate its concentration in terms of experimental quantities. Thus

$$R_i = R_t$$

$$Kk_i[Cat][M] = k_t[complex][NH_3]$$

$$[complex] = \frac{Kk_i[Cat][M]}{k_t[NH_3]}$$

Putting this value in equation (13.79)

$$R_P = k_P \frac{Kk_i}{k_t} \frac{[Cat][M]^2}{[NH_3]}$$

The average degree of polymerization is given by

$$\bar{X}_n = \frac{R_P}{R_t} = \frac{k_p[complex][M]}{k_t[complex][NH_3]}$$

$$\bar{X}_n = \frac{k_p[M]}{k_t[NH_3]}$$

Anionic initiation reactions are much more complicated and the mechanisms proposed are specific for each catalyst.

Example 13.4

If $\overline{M}_n$ of polymer of glycol and 1,2-ethandiamine is 25,000 g/mol, then calculate its degree of polymerization.

Solution

Number average molecular weight = $\overline{M}_n = 25{,}000$ g/mol

Molecular mass of water= $M_w = 18$ g/mol

Molecular mass of repeating unit = $M_r = 86$ g/mol

Degree of polymerization = n = ?

Polymerization reaction is

$$HOC_2H_4OH + H_2NC_2H_4NH_2 \xrightarrow{-nH_2O} HO(C_2H_4HNC_2H_4NH)_n\,H$$

Molecular weight of polymer = $(86 \times n) + 18$

$$25000 = (86 \times n) + 18$$
$$86 \times n = 24982$$
$$n = 290.48$$

13.6 COPOLYMERIZATION

That type of polymer which is made up of two monomers is called copolymer. The process by which copolymer is synthesize known as copolymerization.

13.6.1 Classification of Copolymers

On the basis of arrangement of monomeric units in copolymer, copolymers are divided five different classes. Structure of all classes is different from each other. Classification scheme and structure of each class is shown in Fig. 13.10 while their detail is as follows

(i) Statistical Copolymer: If arrangement of monomeric units in copolymer is completely according to statistical laws, then that copolymer is termed as statistical copolymer.

(ii) Alternate Copolymer: If two monomeric units successively alternate each other in polymer, then it is alternate copolymer.

(iii) Random Copolymer: These copolymers have no specific pattern of arrangement of monomeric units.

(iv) Graft Copolymer: That branched copolymer in which one monomeric unit forms backbone and other forms branches attached to this backbone is known as graft copolymer.

(v) **Block Copolymer:** Many monomeric units of one type combine and form block. Later these blocks of both monomeric units get arranged linearly and form block copolymer.

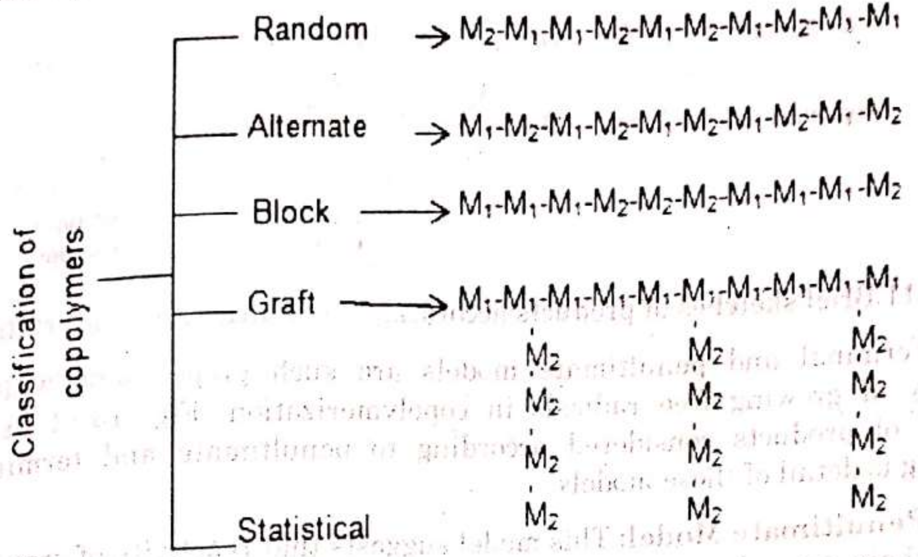

Classification of copolymers
Random
→ M2-M1-M1-M2-M1-M2-M1-M2-M1-M1
Alternate
→ M1-M2-M1-M2-M1-M2-M1-M2-M1-M2
Block
→ M1-M1-M1-M2-M2-M2-M1-M1-M1-M2
Graft
→ M1-M1-M1-M1-M1-M1-M1-M1-M1-M1
M2
M2
M2
M2
Statistical

Fig. 13.10 Classification of copolymers along with sketch of structure of each class of copolymer

13.6.2 Kinetics of Copolymerization

Copolymerization can occur through step as well as chain growth polymerization. It depends upon monomers whether they prefer step growth or chain growth. Here we use free radical chain growth polymerization to explain kinetics of copolymerization. Initiation and termination are same as discussed before while propagation is different in copolymerization.

Let M_1 and M_2 are two commoners involved in copolymerization and $\dot{M}_1$ and $\dot{M}_2$ are their growing radicals respectively. Growing radicals may has $\dot{M}_1$ or $\dot{M}_2$ as growing end group in binary mixture. So there are four possible propagation reactions because there are equal chances for $\dot{M}_1$ to bind with M_1 or M_2 and vice versa for $\dot{M}_2$ radicals.

Reaction I: $\dot{M}_1$ binds with M_1, so terminal reactive end group and penultimate specie is of M_1. k_{11} is rate constant of self addition of $\dot{M}_1$ to M_1.

Reaction II: $\dot{M}_1$ binds with M_2 and product has terminal reactive end group and penultimate specie of M_2 and M_1 respectively. k_{12} is rate constant of $\dot{M}_1$ addition to M_2.

Reaction III: Here $\dot{M}_2$ binds with M_2, and product has terminal reactive group and penultimate specie of M_2. k_{22} is rate constant of self addition of $\dot{M}_2$ to M_2.

Reaction IV: $\dot{M}_2$ binds with M_1, product has reactive end group of M_1 and penultimate specie of M_2. k_{21} is rate constant of $\dot{M}_2$ addition to M_1

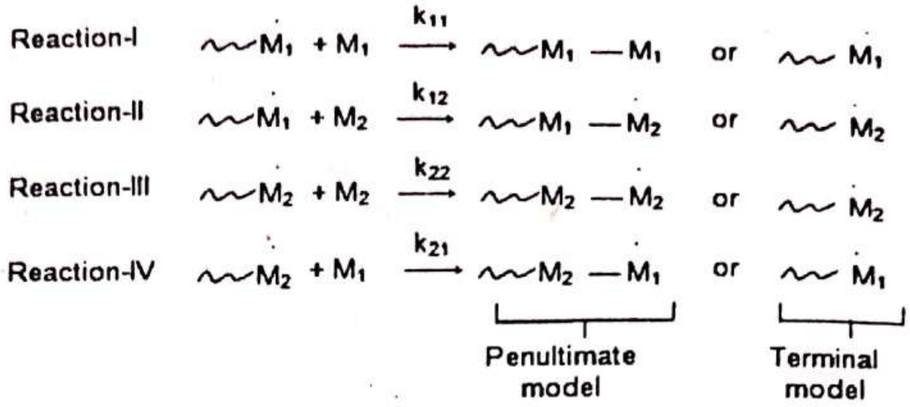

Reaction-I
$\sim\sim\dot{M}_1 + M_1 \xrightarrow{k_{11}} \sim\sim M_1 - \dot{M}_1$ or $\sim\sim \dot{M}_1$
Reaction-II
$\sim\sim\dot{M}_1 + M_2 \xrightarrow{k_{12}} \sim\sim M_1 - \dot{M}_2$ or $\sim\sim \dot{M}_2$
Reaction-III
$\sim\sim\dot{M}_2 + M_2 \xrightarrow{k_{22}} \sim\sim M_2 - \dot{M}_2$ or $\sim\sim \dot{M}_2$
Reaction-IV
$\sim\sim\dot{M}_2 + M_1 \xrightarrow{k_{21}} \sim\sim M_2 - \dot{M}_1$ or $\sim\sim \dot{M}_1$
Penultimate model
Terminal model

Fig. 13.11 Brief sketches of products according to penultimate and terminal models

Terminal and penultimate models are such propositions which describe reactivity of growing free radicals in copolymerization. Fig. 13.11 exhibits brief sketches of products considered according to penultimate and terminal models. Following is detail of these models

(i) **Penultimate Model:** This model suggests that reactivity of growing polymer chain depends upon last two units of chain. It means reactivity of products of reaction-I and reaction-IV are not equally reactive for further propagation of chain and vice versa for products of reaction-II and reaction III.

(ii) **Terminal Model:** This model proposed that reactivity of growing polymer chain only depends upon last unit of chain. It means reactivity of product of reaction-I and reaction-IV, and products of reaction-II and reaction III have equal reactivity for further propagation of chain.

We discuss kinetics of copolymerization within perspective of terminal model as

(a) It is not so complicated to describe.

(b) It gives general principle by which most of the copolymerizations have been explained successfully.

By accepting general propositions of terminal model, following fruitful conclusions from some suitable limitations can be successfully drawn

Case I $k_{11}>>k_{12}$ and $k_{22}>>k_{21}$

If case-I is applicable, then terminal reactive group prefers self addition of monomers and block copolymer polymerized. If $k_{11}>>>>k_{12}$ and $k_{22}>>>>k_{21}$, then homopolymer may formed because there is much greater tendency of self addition of monomers which may not give a single chance to bind with monomer of other kind.

Case II $k_{12}>>k_{11}$ and $k_{21}>>k_{22}$

Under these conditions, growing polymer chain of one type prefers to bind with monomer of other type, thus alternate copolymer is formed.

Case II I $k_{12}=k_{11}$ and $k_{21}=k_{22}$

Now, growing polymer chain of one type has equal tendency to bind with both monomers. Thus random copolymer is formed.

Detail study of kinetics according to terminal model is as follows

Reaction I $\dot{M}_1 + M_1 \xrightarrow{k_{11}} \dot{M}_1$

Rate of reaction-I is equal to rate of consumption of M_1, as

$$R_I = -\frac{d[M_1]}{dt} = k_{11}[\dot{M}_1][M_1] \tag{13.80}$$

Reaction II $\dot{M}_1 + M_2 \xrightarrow{k_{12}} \dot{M}_2$

Rate of reaction-II is equal to rate of consumption of M_2, as

$$R_{II} = -\frac{d[M_2]}{dt} = k_{12}[\dot{M}_1][M_2] \tag{13.81}$$

Reaction III $\dot{M}_2 + M_2 \xrightarrow{k_{22}} \dot{M}_2$

Rate of reaction-III is equal to rate of consumption of M_2, as

$$R_{III} = -\frac{d[M_2]}{dt} = k_{22}[\dot{M}_2][M_2] \tag{13.82}$$

Reaction IV $\dot{M}_2 + M_1 \xrightarrow{k_{21}} \dot{M}_1$

Rate of reaction-IV is equal to rate of consumption of M_1, as

$$R_{IV} = -\frac{d[M_1]}{dt} = k_{21}[\dot{M}_2][M_1] \tag{13.83}$$

Monomer M_1 is consumed during reaction-I and IV, so

$$-\frac{d[M_1]}{dt} = R_I + R_{IV}$$

Thus, equations (13.80) and (13.83) are used to write equation for rate total of consumption of M_1

$$-\frac{d[M_1]}{dt} = k_{11}[\dot{M}_1][M_1] + k_{21}[\dot{M}_2][M_1] \tag{13.84}$$

Monomer M_2 is consumed during reactions II and III, so

$$-\frac{d[M_1]}{dt} = R_{II} + R_{III}$$

Thus, equations (13.81) and (13.82) are used to write equation for rate total of consumption of M_1

$$-\frac{d[M_2]}{dt} = k_{22}[\dot{M}_2][M_2] + k_{12}[\dot{M}_1][M_2] \tag{13.85}$$

Dividing equation (13.84) by (13.85)

$$\frac{d[M_1]}{d[M_2]}=\frac{k_{11}[\dot{M}_1][M_1]+k_{21}[\dot{M}_2][M_1]}{k_{22}[\dot{M}_2][M_2]+k_{12}[\dot{M}_1][M_2]}$$

Divide and multiply above equation by $[\dot{M}_2]$

$$\frac{d[M_1]}{d[M_2]}=\frac{[\dot{M}_2]}{[\dot{M}_2]}\left(\frac{k_{11}[\dot{M}_1][M_1]+k_{21}[\dot{M}_2][M_1]}{k_{22}[\dot{M}_2][M_2]+k_{12}[\dot{M}_1][M_2]}\right)$$

$$\frac{d[M_1]}{d[M_2]}=\frac{k_{11}[M_1]\dfrac{[\dot{M}_1]}{[\dot{M}_2]}+k_{21}[M_1]\dfrac{[\dot{M}_2]}{[\dot{M}_2]}}{k_{22}[M_2]\dfrac{[\dot{M}_2]}{[\dot{M}_2]}+k_{12}[M_2]\dfrac{[\dot{M}_1]}{[\dot{M}_2]}}$$

$$\frac{d[M_1]}{d[M_2]}=\frac{k_{11}[M_1]\dfrac{[\dot{M}_1]}{[\dot{M}_2]}+k_{21}[M_1]}{k_{22}[M_2]+k_{12}[M_2]\dfrac{[\dot{M}_1]}{[\dot{M}_2]}} \qquad (13.86)$$

$\dot{M}_2$ and $\dot{M}_1$ are two principal radicals present in reaction mixture. As polymerization is a fast process, so steady state condition tells that net concentration of $\dot{M}_1$ and $\dot{M}_2$ is zero in reaction. It means rate of formation of $\dot{M}_1$ is equal to rate of consumption of $\dot{M}_1$ and vice versa for $\dot{M}_2$. Thus rates of reaction-II and IV are equal, and rates of reactions I and III are equal. Self addition reactions of $\dot{M}_2$ and $\dot{M}_1$ are not considered here as product and reactant are same species. So

$$R_{IV}=R_{II}$$

$$k_{21}[\dot{M}_2][M_1]=k_{12}[\dot{M}_1][M_2]$$

$$\frac{[\dot{M}_1]}{[\dot{M}_2]}=\frac{k_{21}[M_1]}{k_{12}[M_2]} \qquad (13.87)$$

Substituting equation (13.87) into equation (13.86)

$$\frac{d[M_1]}{d[M_2]}=\frac{k_{11}[M_1]\dfrac{k_{21}[M_1]}{k_{12}[M_2]}+k_{21}[M_1]}{k_{22}[M_2]+k_{12}[M_2]\dfrac{k_{21}[M_1]}{k_{12}[M_2]}}$$

$$\frac{d[M_1]}{d[M_2]} = \frac{k_{21}\dfrac{k_{11}[M_1]^2}{k_{12}[M_2]} + k_{21}[M_1]}{k_{22}[M_2] + k_{21}[M_1]}$$

Dividing nominator as well as denominator of above equation with $k_{21}[M_1]$

$$\frac{d[M_1]}{d[M_2]} = \frac{\dfrac{k_{21}}{k_{21}}\dfrac{k_{11}[M_1]^2}{k_{12}[M_2][M_1]} + \dfrac{k_{21}[M_1]}{k_{21}[M_1]}}{\dfrac{k_{22}[M_2]}{k_{21}[M_1]} + \dfrac{k_{21}[M_1]}{k_{21}[M_1]}}$$

$$\frac{d[M_1]}{d[M_2]} = \frac{\dfrac{k_{11}[M_1]}{k_{12}[M_2]} + 1}{\dfrac{k_{22}[M_2]}{k_{21}[M_1]} + 1} \qquad (13.88)$$

Reactivity ratios r_1 and r_2 are

$$r_1 = \frac{k_{11}}{k_{12}}$$

and $$r_2 = \frac{k_{22}}{k_{21}}$$

Substituting reactivity ratios r_1 and r_2 from previous both equations into (13.88)

$$\frac{d[M_1]}{d[M_2]} = \frac{r_1\dfrac{[M_1]}{[M_2]} + 1}{r_2\dfrac{[M_2]}{[M_1]} + 1} \qquad (13.89)$$

Equation (13.89) is a copolymer composition equation which gives concentration of monomer M_1 polymerized with respect to concentration of monomer M_2 in time dt. Using this equation we can determine feed ratio of monomers ($[M_1]/[M_2]$) into polymer, as it is generally assumed that feed ratio of mixture is equal to feed ratio of polymer.

It is always not necessary to mention data in terms of feed ratio, term of mole fraction is also used. Monomers are continuously depleting from reaction and incorporated into polymer, so F_1 and F_2 are mole fractions of monomer M_1 and M_2 into polymer, while their mole fractions left in reaction mixture are f_1 and f_2. So

$$F_2 + F_1 = 1 \qquad (13.90)$$

$$F_1 = 1 - F_2 = \frac{d[M_1]}{d[M_1] + d[M_2]} \qquad (13.91)$$

$$F_2 = 1 - F_1 = \frac{d[M_2]}{d[M_1] + d[M_2]} \tag{13.92}$$

and

$$f_2 + f_1 = 1 \tag{13.93}$$

$$f_1 = 1 - f_2 = \frac{[M_1]}{[M_1] + [M_2]} \tag{13.94}$$

$$f_2 = 1 - f_1 = \frac{[M_2]}{[M_1] + [M_2]} \tag{13.95}$$

To correlate mole fractions of monomers incorporating into polymer and left in mixture, we modify equation (13.89) as

Multiply nominator and denominator of equation (13.89) with $[M_1][M_2]$

$$\frac{d[M_1]}{d[M_2]} = \frac{r_1[M_1][M_2]\dfrac{[M_1]}{[M_2]} + [M_1][M_2]}{r_2[M_1][M_2]\dfrac{[M_2]}{[M_1]} + [M_1][M_2]}$$

$$\frac{d[M_1]}{d[M_2]} = \frac{r_1[M_1]^2 + [M_1][M_2]}{r_2[M_2]^2 + [M_1][M_2]}$$

Rearranging above equation

$$\frac{d[M_2]}{d[M_1]} = \frac{r_2[M_2]^2 + [M_1][M_2]}{r_1[M_1]^2 + [M_1][M_2]}$$

Add 1 on both sides of above equation

$$\frac{d[M_2]}{d[M_1]} + 1 = \frac{r_2[M_2]^2 + [M_1][M_2]}{r_1[M_1]^2 + [M_1][M_2]} + 1$$

$$\frac{d[M_1] + d[M_2]}{d[M_1]} = \frac{r_2[M_2]^2 + [M_1][M_2] + r_1[M_1]^2 + [M_1][M_2]}{r_1[M_1]^2 + [M_1][M_2]}$$

Now substituting F_1 from equation (13.91) into above equation

$$\frac{1}{F_1} = \frac{r_2[M_2]^2 + 2[M_1][M_2] + r_1[M_1]^2}{r_1[M_1]^2 + [M_1][M_2]}$$

Divide nominator and denominator of above equation with $([M_1]+[M_2])^2$

$$\frac{1}{F_1} = \frac{r_2\frac{[M_2]^2}{([M_1]+[M_2])^2} + 2\frac{[M_1][M_2]}{([M_1]+[M_2])^2} + r_1\frac{[M_1]^2}{([M_1]+[M_2])^2}}{r_1\frac{[M_2]^2}{([M_1]+[M_2])^2} + \frac{[M_1][M_2]}{([M_1]+[M_2])^2}}$$

Substituting f_1 and f_2 from equation (13.94) and (13.95) into above equation

$$\frac{1}{F_1} = \frac{r_2 f_2^2 + 2f_1^2 f_2^2 + r_1 f_1^2}{r_1 f_2^2 + f_1 f_2}$$

or

$$F_1 = \frac{r_1 f_2^2 + f_1 f_2}{r_2 f_2^2 + 2f_1^2 f_2^2 + r_1 f_1^2} \qquad (13.96)$$

and

$$1 - F_2 = \frac{r_1 f_2^2 + f_1 f_2}{r_2 f_2^2 + 2f_1^2 f_2^2 + r_1 f_1^2}$$

$$F_2 = 1 - \frac{r_1 f_2^2 + f_1 f_2}{r_2 f_2^2 + 2f_1^2 f_2^2 + r_1 f_1^2} \qquad (13.97)$$

Equations (13.96) and (13.97) give amounts of monomers into reaction mixture and polymer at different mole fractions.

13.6.3 Reactivity Ratios and Composition of Polymer

Reactivity ratios r_1 and r_2 are useful to predict nature of copolymer formed. Following are some special cases and their immediate predictions

Special Case I: $r_1 = r_2 = 0$

This is possible when k_{11} and k_{22} are zero and k_{12} and k_{21} are not zero, it means tendency for self addition of monomers is negligible while tendency to add monomer of other type is significant. So both monomers are alternatively add into polymer and a perfect alternate copolymer is fabricated.

Special Case II: $r_1 = r_2 = \infty$

This is possible when k_{12} and k_{22} are zero, accordingly there is large tendency for self addition of monomers as compared to addition of monomer of other kind. So homopolymers are formed.

Special Case III: $r_1 = r_2 = 1$

Now k_{11}, k_{22}, k_{12} and k_{21} are equal, so a competition develops between self addition and non-self addition of monomers. Under such conditions, random copolymer is synthesized.

Special Case IV: $r_1 r_2 = 1$

This is case of ideal copolymerization, under this condition copolymer is truly random but this condition does not prevail mostly due to side reactions and non-ideal reaction conditions.

Example 13.5

If feed ratio of styrene and maleic anhydride is 3:1 and reactivity ratios of styrene and maleic anhydride are 2 and 0.25 respectively, then calculate composition of copolymer.

Solution

Concentration of styrene = $[M_1] = 3\,[M_2]$

Concentration of maleic anhydride = $[M_2]$

Reactivity ratio of styrene = $r_1 = 2$

Reactivity ratio of styrene = $r_2 = 0.25$

Composition of copolymer= $d[M_1]/d[M_2]$ = ?

Using copolymer composition equation, we have

$$\frac{d[M_1]}{d[M_2]} = \frac{r_1\frac{[M_1]}{[M_2]}+1}{r_2\frac{[M_2]}{[M_1]}+1} = \frac{2\times\frac{3[M_2]}{[M_2]}+1}{0.25\times\frac{[M_2]}{3[M_2]}+1} = \frac{2\times3+1}{\frac{0.25}{3}+1} = \frac{7}{0.083+1} = 6.46$$

13.7 MOLECULAR WEIGHT AVERAGES

Molecular weight of a polymer cannot have a single value as all chains of polymer synthesized at one time are not equal in length. Thus for this kind of polydisperse system average molecular weight is quoted. Viscosity average, z-average, number average and weight average molecular weights are different molecular weights which can be determined different methods. A single method of characterization cannot measure all kinds of weight averages.

(i) Number Average Molecular Weight

Number average molecular weight ($\overline{M}_n$) is summation of all fractions of polymers multiplied by their molecular masses. Let f_1 is fraction of molecules of mass M_1, f_2 is fraction of molecules of mass M_2 and so on.

$$\overline{M}_n = f_1M_1 + f_2M_2 + f_2M_2 + ... + f_iM_i$$

Generally it can be written as

$$\overline{M}_n = \Sigma_i f_iM_i \qquad (13.98)$$

If N_i is number of molecules of fraction of molecules f_i, and N_{Total} is total number of molecules, then :

$$f_i = \frac{N_i}{N_{Total}} \qquad (13.99)$$

where $N_{Total} = \Sigma_i N_i$

Putting value from equation (13.99) into (13.98) as

$$\overline{M}_n = \frac{\Sigma_i N_i M_i}{N_{Total}} \qquad (13.100)$$

Equation (13.100) gives formula for calculation of $\overline{M}_n$.

(ii) Mass Average Molecular Weight

Mass average molecular weight ($\overline{M}_m$) is calculated by summation of all mass fractions multiplied by their respective molecular masses. Let w_1 is mass fraction of molecules of molar mass M_1, w_2 is fraction of molecules of molar mass M_2 and so on.

$$\overline{M}_m = w_1M_1 + w_2M_2 + w_2M_2 + ... + w_iM_i$$

Generally it can be written as

$$\overline{M}_m = \Sigma_i w_i M_i \qquad (13.101)$$

If m_i is mass of molecules having molar mass M_i, and m_{Total} is total mass of sample of polymer, then

$$w_i = \frac{m_i}{m_{Total}} \qquad (13.102)$$

Where, $m_{Total} = \Sigma_i m_i$

Substituting value from equation (13.102) into (13.101) as

$$\overline{M}_n = \frac{\Sigma_i m_i M_i}{m_{Total}}$$

$$\overline{M}_m = \frac{\Sigma_i m_i M_i}{\Sigma_i m_i}$$

We know that

$$m_i = \frac{\Sigma_i N_i M_i}{N_A}$$, hence above equation will be

$$\overline{M}_m = \frac{\Sigma_i \frac{N_i M_i}{N_A} M_i}{\Sigma_i \frac{N_i M_i}{N_A}}$$

$$\overline{M}_m = \frac{\Sigma_i N_i M_i M_i}{\Sigma_i N_i M_i}$$

$$\overline{M}_m = \frac{\sum_i N_i M_i^2}{\sum_i N_i M_i} \tag{13.103}$$

Equation (13.103) gives formula for calculation of $\overline{M}_m$. $\overline{M}_m > \overline{M}_n$ is applicable for polydisperse system, since longer chain has greater mass, so it can greatly enhance $\overline{M}_m$, while it is very rare that a large number of chains of single fraction is present.

(iii) z-Average Molecular Weight

z-average molecular weight ($\overline{M}_z$) is

$$\overline{M}_z = \frac{\sum_i N_i M_i^3}{\sum_i N_i M_i^2} \tag{13.104}$$

Equation (13.104) gives formula for calculation of $\overline{M}_z$. $\overline{M}_z > \overline{M}_m > \overline{M}_n$, this trend exists because weighing factor is $N_iM_i^2$ in $\overline{M}_z$.

Other Molecular Weight Averages

Viscosity and z+1 average molecular weights are also used in various experiments.

(i) Viscosity Average Molecular Weight

Following equation is used for determination of viscosity average molecular weight

$$\overline{M}_v = \left(\frac{\sum_i N_i M_i^{\alpha+1}}{\sum_i N_i M_i}\right)^{1/\alpha}$$

Where α is constant used in Mark-Howink-Sakurada equation. Value of α usually vary between 0.5 and 1.

(ii) z+1 Average Molecular Weight

Following equation is used for determination of viscosity average molecular weight

$$\overline{M}_{z+1} = \frac{\sum_i N_i M_i^4}{\sum_i N_i M_i^3}$$

We have following general expression of molecular weight

$$\overline{M} = \frac{\sum_i N_i M_i^{\alpha+1}}{\sum_i N_i M_i^{\alpha}}$$

When $\alpha=0$, then $\overline{M} = \overline{M}_n$

When $\alpha=1$, then $\overline{M} = \overline{M}_w$

When $\alpha=2$, then $\overline{M} = \overline{M}_z$

When $\alpha=3$, then $\overline{M} = \overline{M}_{z+1}$

Distribution of Average Molecular Weights

For any molecular weight distribution, following order persists among various average molecular weights

$$\overline{M}_n \le \overline{M}_v \le \overline{M}_w \le \overline{M}_z \le \overline{M}_{z+1}$$

All weight averages are equal when polymer is monodisperse. But they become unequal and obey above order when polymer is polydisperse. Different terms of average molecular weights have made communication among scientists comparatively easy. If a scientist determine molecular weight of a polydisperse system of polymer by light scattering then he can report it as $\overline{M}_w$ rather simply saying it molecular weight. Similarly other scientist determine weight of same polymer by osmometry then he can report it as $\overline{M}_n$. Both these scientists obtained different values of the same polymer because $\overline{M}_n$ is different from $\overline{M}_w$. So conflict between their reported values vanishes.

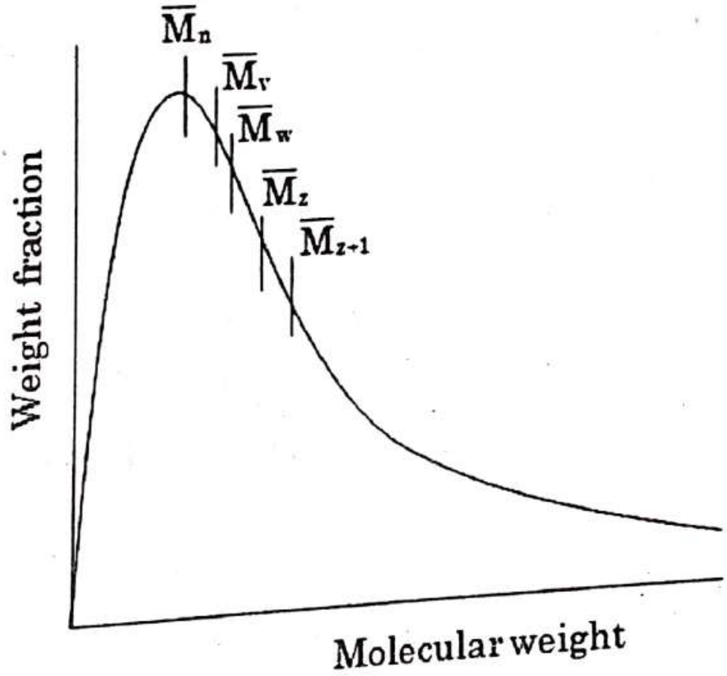


Fig. 13.12 Schematic plot of distribution of molecular weights along with ranking of various average molecular weights.

Average Degree of Polymerization

The degree of polymerization is the number of monomer units in a given polymer molecule. Since there is distribution of molecular weight in polymer sample. The chain lengths of polymer molecules will vary and hence the degree of polymerization will vary, so one must speak of an average degree of polymerization.

A. Number Average Degree of Polymerization ($\overline{X}_n$)

It is the number of monomer units in the chain of number average molecular weight, so

$$\overline{X}_n = \frac{\overline{M}_n}{M_o}$$

Where M_o is the molecular weight of repeating unit in the chain.

B. Weight Average Degree of Polymerization ($\overline{X}_w$)

It is the number of monomer units in the chain of weight average molecular weight, so

$$\overline{X}_n = \frac{\overline{M}_w}{M_o}$$

For high molecular weight polymers, value of $\overline{X}_n$ and $\overline{X}_w$ will be very large.

Example 13.6

Sample A of polymer is polydisperse. 4, 8, 1 and 3 chains have weight 10,000, 2,000, 5,000 and 15,000 lb/mol respectively. Calculate $\overline{M}_n$, $\overline{M}_m$ and $\overline{M}_z$ and compare their values.

Solution

Number of chains having weight 10,000 lb/mol=4

Number of chains having weight 2,000 lb/mol=8

Number of chains having weight 5,000 lb/mol=1

Number of chains having weight 15,000 lb/mol=3

Using equation (13.87), (13.90) and (13.91), we calculate $\overline{M}_n$, $\overline{M}_m$ and $\overline{M}_z$ as

(i)
$$\overline{M}_n = \frac{\Sigma_i N_i M_i}{N_{Total}} = \frac{(4\times10000)+(8\times2000)+(1\times5000)+(3\times15000)}{(4+8+1+3)}$$

$$\overline{M}_n = \frac{40000+16000+5000+45000}{16} = \frac{106000}{16} = 6.625\times10^3\ \text{lb/mol}$$

(ii)
$$\overline{M}_m = \frac{\Sigma_i N_i M_i^2}{\Sigma_i N_i M_i}$$

$$\overline{M}_m = \frac{\left(4\times(10000)^2\right)+\left(8\times(2000)^2\right)+\left(1\times(5000)^2\right)+\left(3\times(15000)^2\right)}{(4\times10000)+(8\times2000)+(1\times5000)+(3\times15000)}$$

$$\overline{M}_m = \frac{(4\times10^8)+(32\times10^6)+(25\times10^6)+(675\times10^6)}{106000} = \frac{1.132\times10^9}{106000}$$

$$\overline{M}_m = 10.6\times10^3\ \text{lb/mol}$$

(iii)

$$\overline{M}_z = \frac{\Sigma_i N_i M_i^3}{\Sigma_i N_i M_i^2}$$

$$\overline{M}_z = \frac{\left(4\times(10000)^3\right)+\left(8\times(2000)^3\right)+\left(1\times(5000)^3\right)+\left(3\times(15000)^3\right)}{\left(4\times(10000)^2\right)+\left(8\times(2000)^2\right)+\left(1\times(5000)^2\right)+\left(3\times(15000)^2\right)}$$

$$\overline{M}_z = \frac{\left(4\times10^{12}\right)+\left(64\times10^{9}\right)+\left(125\times10^{9}\right)+\left(10125\times10^{9}\right)}{\left(4\times10^{8}\right)+\left(32\times10^{6}\right)+\left(25\times10^{6}\right)+\left(675\times10^{6}\right)} = \frac{1.4314\times10^{13}}{1.132\times10^{9}}$$

$$\overline{M}_z = 12.64\times10^3 \text{ lb/mol}$$

Calculates values shows that

$$\overline{M}_z\left(12.64\times10^3 \text{ lb/mol}\right) > \overline{M}_m\left(10.6\times10^3 \text{ lb/mol}\right) > \overline{M}_n\left(4\times10^3 \text{ lb/mol}\right)$$

13.8 MOLECULAR MASS DETERMINATION METHODS

Osmometry, viscometry, light scattering and sedimentation methods are commonly used methods for determination of molar mass of a polymer. Some methods are given here in detail.

13.8.1 Viscosity Method

Viscosity of a fluid is a fundamental property which has been described in section 11.11. Viscosity measurements can be used for determination of molar mass of a polymer. Ostwald viscometer is the simplest apparatus which is used for measurement of viscosity of a solution. Ostwald viscometer consists of a bulb B with markings x_1 and x_2 attached to a capillary tube C and a reservoir D as shown in Fig. 13.13. A liquid is introduced from C and sucked from B side. Then time of flow of liquid from x_1 to x_2 is recorded. The value of relative viscosity can be measured using following formula.

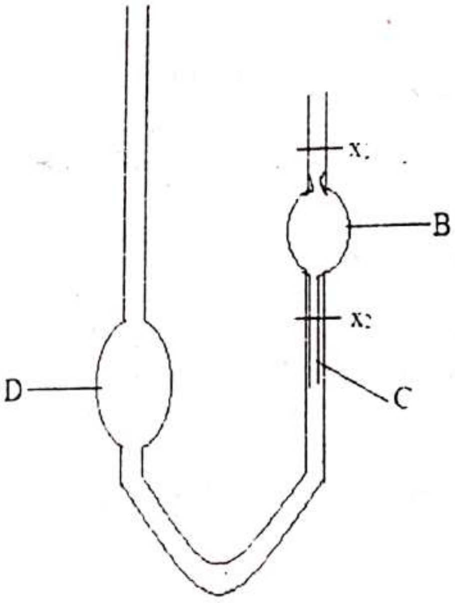


Fig. 13.13 Ostwald viscometer

$$\eta_{rel} = \frac{\eta}{\eta_0} = \frac{\rho}{\rho_0}\cdot\frac{t}{t_0}$$

Where,

η = viscosity of solution

η_0 = viscosity of solvent

t = time of flow of solution

t_0 = time of flow of solvent

ρ = density of solution

ρ_0 = density of solvent

Time flow can be measured by Ostwald viscometer while densities can be determined by filling gravity bottle. Specific viscosity is obtained from relative viscosity using the following relation.

$$\eta_{sp} = \eta_{rel} - 1$$

The specific viscosity is converted into reduced viscosity by the relation

$$\eta_{red} = \frac{\eta_{sp}}{C}$$

Where, C is the concentration in gmL^{-1}.

$\frac{\eta_{sp}}{C}$ is plotted as a function of concentration of polymer as shown in Fig. 13.14. The intercept of the plot is viscosity of the solution at infinite dilution and it is called intrinsic viscosity i.e.

$$\text{Intrinsic viscosity} = [\eta] = Lim_{c \to 0} \frac{\eta_{sp}}{C}$$

The relation between $[\eta]$ and molar mass of a polymer is given by the equation

$$[\eta] = KM^{\alpha}$$

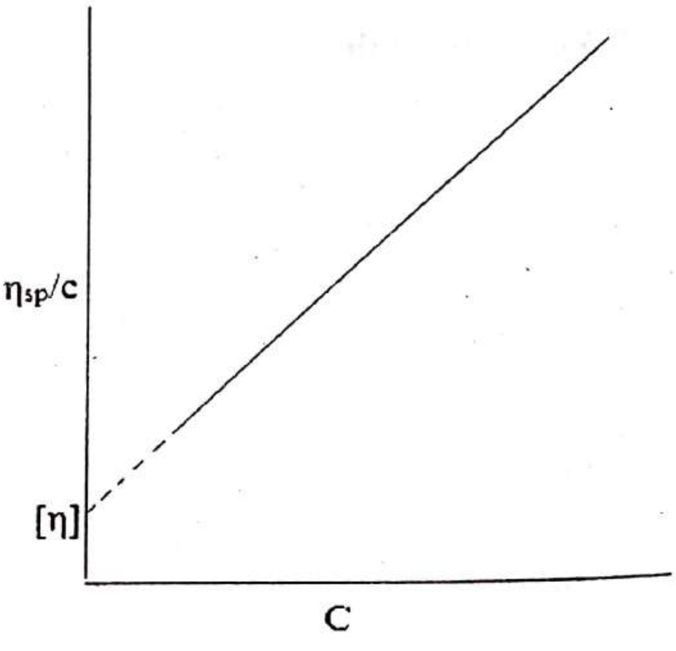


Fig. 13.14 Plot of η_{sp}/c as a function of concentration.

Where, α and K are empirical constants and M is the molar mass of polymer. The above equation can be used for determination of molar mass of polymer for which K and α are known.

13.8.2 Sedimentation

Let us consider a particle of polymer in solution which moves under the influence of gravitational field. The falling particle having mass m_s experiences a centrifugal force which is equal to $\omega^2 r m$ and buoyancy force. The net force acting on the particle can be written as

Net force = centrifugal force – buoyancy force

$$= \frac{mv^2}{r} - \omega^2 r m_s$$

$$= \frac{m(r\omega)^2}{r} - \omega^2 r m_s$$

$$= \frac{mr^2\omega^2}{r} - \omega^2 r m_s$$

$$= mr\omega^2 - \omega^2 r m_s \qquad (13.105)$$

Where, ω is the angular velocity of the rotor in radius per second, r is the distance from centre of rotation of particle.

As we know that $m_s = \rho v$, by putting this value in equation (13.105),

$$= mr\omega^2 - \omega^2 r\rho v$$

So, net force will be equal to frictional force

$$f\left(\frac{dr}{dt}\right) = mr\omega^2 - \omega^2 r\rho v$$

$$f\left(\frac{dr}{dt}\right) = mr\omega^2 - \omega^2 r\rho m\left(\frac{v}{m}\right)$$

$$f\left(\frac{dr}{dt}\right) = mr\omega^2 - \omega^2 r\rho m\bar{v}$$

$$f\left(\frac{dr}{dt}\right) = \omega^2 mr\left(1 - \rho\bar{v}\right)$$

$$\left(\frac{dr}{dt}\right) = \frac{\omega^2 mr\left(1 - \rho\bar{v}\right)}{f}$$

$$\frac{\frac{dr}{dt}}{\omega^2 r} = \frac{N_A m\left(1 - \rho\bar{v}\right)}{N_A f}$$

Where, $\bar{v}$ is the partial specific volume, dr/dt is the sedimentation velocity. Left hand side is replaced by S because the term $\frac{dr/dt}{\omega^2 r}$ is the sedimentation coefficient (S). N_A is Avogadro's number.

$$S = \frac{M(1-\rho\bar{v})}{N_A f}$$

$$M = \frac{SN_A f}{1-\rho\bar{v}} \tag{13.106}$$

According to Stoke's law frictional coefficient of a spherical particle is

$$f = 6\pi\eta r_s$$

By putting value of f in equation (13.106), we get

$$M = \frac{SN_A(6\pi\eta r_s)}{1-\rho\bar{v}} \tag{13.107}$$

According to Stoke's Einstein equation, we know

$$D = \frac{k_B T}{6\pi\eta r_s}$$

$$6\pi\eta r_s = \frac{k_B T}{D}$$

Where, k_B is the Boltzmann constant, D is the diffusion coefficient and T is the absolute temperature.

By putting value of $6\pi\eta r_s$ in equation (13.107), we get

$$M = \frac{SN_A k_B T}{D(1-\rho\bar{v})}$$

$$M = \frac{SRT}{D(1-\rho\bar{v})}$$

In the above equation, unknown quantities are $\bar{v}$, D and S. $\bar{v}$ and D can be measured by some separate experiments. The sedimentation coefficient can be determined by the following ways.

$$S = \frac{dr/dt}{\omega^2 r}$$

$$Sdt = \frac{1}{\omega^2}\frac{dr}{r}$$

By integrating above equation within limits

$$S\int_0^t dt = \frac{1}{\omega^2}\int_{r_0}^{r}\frac{1}{r}dr$$

$$S(t-0) = \frac{1}{\omega^2}\left|\ln r\right|_{r_0}^{r}$$

$$St = \frac{1}{\omega^2}(\ln r - \ln r_0) \qquad (13.108)$$

$$St = \frac{\ln\left(r/r_0\right)}{\omega^2}$$

$$S = \frac{1}{t\omega^2}\ln\left(r/r_0\right)$$

By rearranging equation (13.108), we get

$$St\omega^2 = \ln r - \ln r_0$$

$$\ln r = St\omega^2 + \ln r_0 \qquad (13.109)$$

Equation (13.109) is an equation of straight line in intercept form as shown in Fig. 13.15 with slope $S\omega^2$. From the slope we can determined the value of sedimentation coefficient.

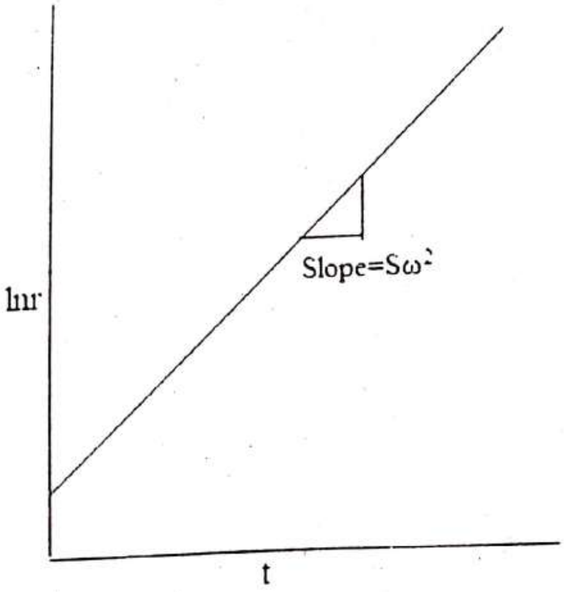


Fig. 13.15 Plot of lnr versus t

13.8.3 Osmometry

Vapour phase and membrane osmometry are two principal types of osmometry used so far to measure number average molecular weight.

(i) Vapour Phase Osmometry

Principle

Addition of solute molecules decreases the vapour pressure of a liquid. Decrease in vapour pressure depends upon number of solute molecules.

Construction and Working

Vapour phase osmometer is shown in Fig. 13.16. Two thermistors are connected to a Wheatstone bridge. Solvent drops were placed in vicinity of both thermistors by using syringes. As both wires are in proximity of same medium as rate of evaporation is same at both wires, so no temperature difference is sensed between both wires and a balance point is established. Now place drop of solution at one thermistor and drop of solvent at the other. Now thermistors detect a temperature difference as rate of evaporation at both ends is unequal. This temperature difference is recorded in terms of potential difference by Wheatstone bridge.

Calculation of Molecular Weight

Output voltage ΔV is related to molecular weight M by following equation

$$\frac{\Delta V}{C} = \frac{K}{\overline{M}_n} + KBC \tag{13.110}$$

K is a calibration constant. Firstly value of K is determined by using polymer of low and known molecular mass having less polydispersity. Then that value of K is used to determine molecular mass. Voltage difference is measured for solutions of different concentrations, then $\Delta V/C$ is plotted against concentration as shown in Fig. 13.16. Value of slope is equal to KB, while value of intercept is equal to $K/\overline{M}_n$. K is known already by calibration, thus $\overline{M}_n$ is determined.

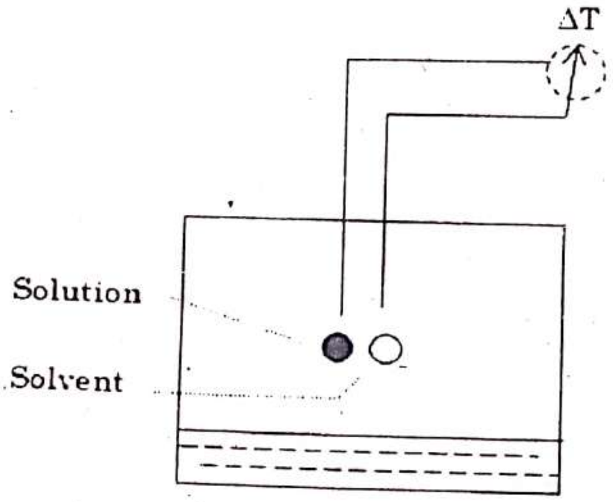


Fig. 13.16 Working of vapour phase osmometry

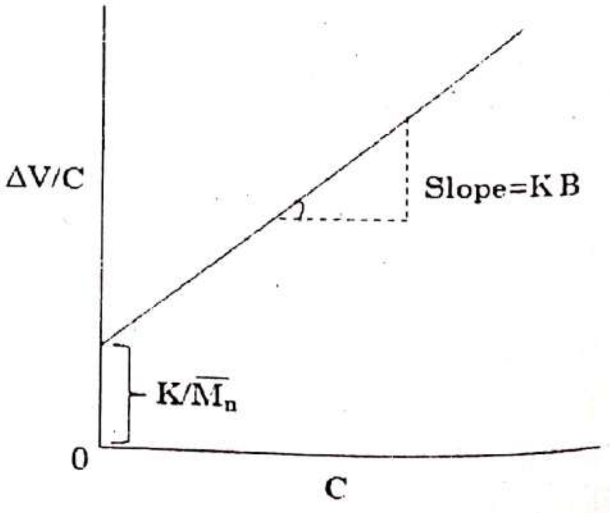


Fig. 13.17 Plot of ΔV/C versus C

Advantages: Quick determination of molecular mass along with use of small amount of polymer is two advantages of this method.

Disadvantages: Only low molecular weight possessing polymers (~30,000) can be successfully measured by it.

(ii) Membrane Osmometry

Principle: Osmotic pressure of solvent decreases by addition of solute molecules. Decrease in osmotic pressure depends upon number of solute molecules and related to molar mass of polymer.

Types: Static, dynamic and high speed membrane osmometers are three kinds of membrane osmometers which are normally use.

(I) **Static Membrane Osmometer:** In this osmometer, both chambers are separated by a membrane and they are individually connected to small capillaries as shown in Fig. 13.18. Initially both chambers contain solvent. So thus there is no net movement of molecules from one chamber to other. So level of liquid in both capillaries is same as shown in Fig. 13.18 (a). Later solution is placed in one chamber while other contains solvent. Now chemical and osmotic potential of both chambers becomes unequal as shown in Fig. 13.18 (b). Now, solvent molecules move from chamber of low osmotic potential towards chamber of higher osmotic potential via semipermeable membrane until equilibrium gets establish. As a result level of liquid in capillary attached to chamber containing solvent becomes low and vice versa for other chamber. Difference in height of liquid in capillary helps to determine osmotic pressure, in return molecular weight also.

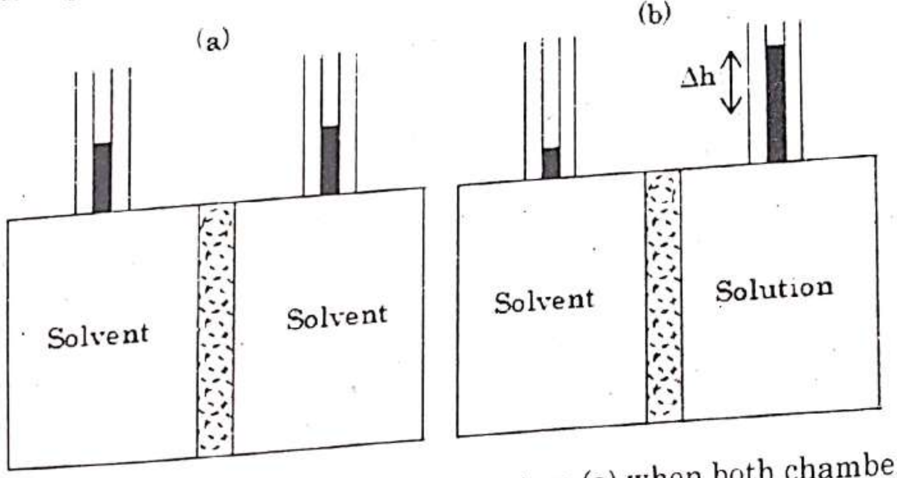


Fig. 13.18 Functioning of membrane osmometers (a) when both chambers have solvent, and (b) when one chamber has solvent while other has solution.

Disadvantages: Time consuming and no membrane is perfectly ideal to completely prevent flow of solute molecules and permit flow of solvent molecules.

(II) **Dynamic Membrane Osmometer:** Here motion of solvent molecules towards chamber of solution is stopped by applying equal and opposite pressure on solution. Thus osmotic pressure is measured in terms that how much pressure has applied to stop flow of solvent molecules.

Advantages: Equilibrium is established soon between both chambers, so it is time saving.

(III) High Speed Membrane Osmometers: Here an optical system is used to monitor flow of solvent molecules through membrane. As soon as solvent molecules starts penetrate into membrane, optical system automatically adjusts pressure by a electro-mechanical device to such level so that no solvent molecules will move.

Advantages: Migration of very small polymer molecules across membrane is perverted, so errors occur in static method do not happen here.

Calculation of Molecular Weight

Van't Hoff law provides basis of osmometry. For osmotic pressure п, we have following relation

$$\frac{\Pi}{C} = RT\left(A_1 + A_2C + A_3C^2 + A_4C^3 \ldots\right)$$

A_1, A_2, A_3 and A_4 are virial coefficients, C is concentration of polymer, R is general gas constant while T is temperature. A_1 equal to $1/\overline{M}_n$, so above equation will be

$$\frac{\Pi}{C} = RT\left(\frac{1}{\overline{M}_n} + A_2C + A_3C^2 + A_4C^3 \ldots\right)$$

For very dilute solutions, above equation will be

$$\frac{\Pi}{C} = RT\left(\frac{1}{\overline{M}_n} + A_2C\right)$$

$$\frac{\Pi}{RTC} = \frac{1}{\overline{M}_n} + A_2C \qquad (13.111)$$

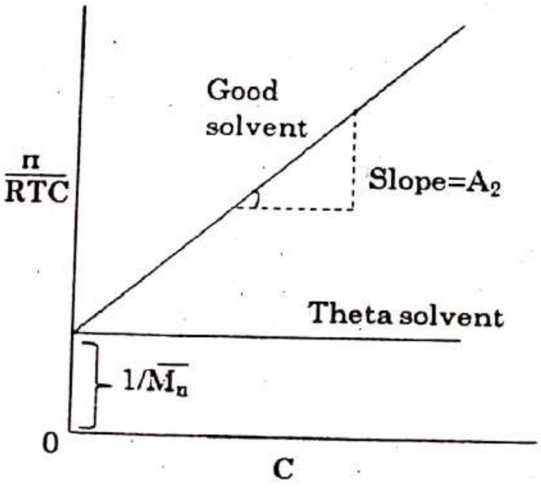


Fig. 13.19 Plot of п/RTC versus C

Following results are drawn from equation (13.111)

(i) Equation (13.98) is a linear equation.

(ii) Plot of π/RTC versus C gives an intercept equal to $1/\overline{M}_n$ and slope equal to A_2 (Fig. 13.18). Thus inverse of intercept gives value of $\overline{M}_n$.

(iii) Value of A_2 is measure of polymer-solvent interactions. High value of slope indicates good polymer-solvent interactions, so that solvent is considered of good quality.

(iv) Low value of slope gives an indication of poor solvent-polymer interactions.

(v) If value of slope is zero, then graph will be parallel to x-axis, and that solvent is considered very poor and called theta solvent.

This is how molecular weight is determined by osmometry.

13.8.4 Light Scattering Measurements

If a beam of light is passed through a colloidal solution, it is possible to see the light beam from sides. This is the well known Tyndall effect which results from the scattering of a part of the beam of light by the colloidal particles in all directions. This principle is used here to determine the weight average molecular weight of polymers.

(a) Light Scattering Measurements from Particles with Diameter Less than λ/20

In the case of macromolecules, the colloidal particles are highly solvated and gel particles consist of about 90 to 99% of the solvent. The refractive index of each colloidal particle is not very different from that of solvent.

According to P. Debye the following power function applies in such cases

$$\Delta\tau = \frac{32\pi^3 RTc}{3\lambda^4 N_A}\left(\frac{n\,dn}{dc}\right)\left(\frac{d\pi}{dc}\right) \qquad (13.112)$$

Where τ is the turbidity, Δτ represents the excess turbidity of the solution over that of the pure solvent, λ is the wavelength of light and n is the refractive index. In the absence of absorption, τ is related to the primary beam intensity before and after it passes through the scattering medium. If the incident intensity I_o is reduced to I in a length ℓ of sample, then

$$\frac{I}{I_o} = e^{-\tau\ell}$$

The turbidity which is the total scattering integral over all angles, is often referred by the Rayleigh ratio $\overline{R}_{(\theta)}$ $[\overline{R}_{(\theta)} = R_{(\theta)} - R_{(\theta)\text{solvent}}]$ which relates the scattered intensity at angle θ to the incident beam intensity. For particles small compared to λ, the Debye equation is obtained as

$$\frac{Kc}{\overline{R}_{(\theta)}} = \frac{Hc}{\tau} = \frac{1}{M} + 2A_2c + \ldots \qquad (13.113)$$

Here K is scattering constant and H is Debye factored. Both are related by following equation

$$K = \frac{3}{16\pi} H$$

and
$$K = \frac{2\pi^2 n^2}{N_A \lambda^4} \left(\frac{dn}{dc}\right)^2$$

$$H = \frac{32\pi^3 n^2}{3N_A \lambda^4} \left(\frac{dn}{dc}\right)^2$$

Equation (13.113) forms the basis of determination of polymer molecular weight by light scattering. Beyond the measurement of τ or $\bar{R}_{(\theta)}$, only the refractive index and the specific refractive index increment (dn/dc) require experimental determination. The latter quantity is constant for a given polymer, solvent and temperature, and is measured with an interferometer or differential refractometer.

Equation (13.113) is correct only for vertically polarized incident light and for optically isotropic particles (in which the refractive index is same in all directions are said to be isotropic e.g. water, glass). The use of unpolarized light requires that τ multiplied by $(1+\cos^2\theta)$.

For system with particles size less than $\lambda/20$, any observation angle may be selected since the scattering function is spherically symmetrical. However for experimental reasons (to avoid interference of primary beam) one usually selects values of θ not very different from 90°.

In this way, through the measurements of scattered light intensity at a single angle, one obtains the molecular weight of particles whose size is less than $\lambda/20$. This is only true for glycogen, proteins and linear polymers of relatively low molecular weights solvated in poor solvents.

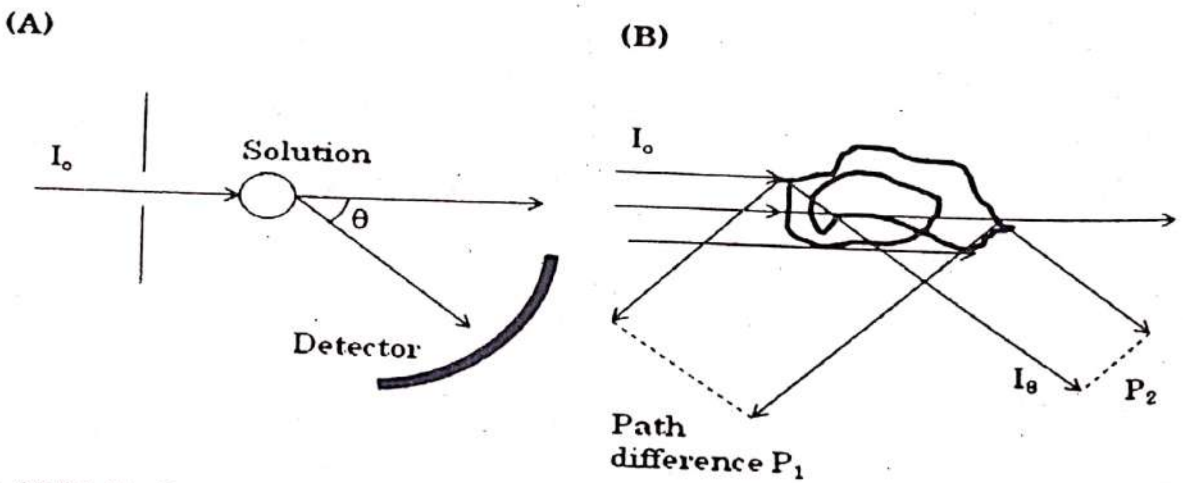


Fig. 13.21 (A) Essential parts of scattering instrument and (B) scattering of light by different parts of large molecule

(a) Light Scattering Measurements from Particles with Diameter Greater than λ/20

For polymer molecules, whose coil diameter is larger than λ/20, the scattering function is no longer spherically symmetrical. Instead one finds a diminution in intensity of scattered light due to interference, which is different at different observation angles. This results from the fact that for larger particles, the different scattering centers within a particle are so far from one another that the resulting scattered rays have a path difference of the order of 0 to λ/20. Since the separate scattering centers within a polymer molecule are activated by one and the same wavelength of primary light, the scattered radiation resulting from the centers is coherent, and therefore capable of interference. The degree of diminution resulting from the interference depends upon the path difference which in turn depends on the angle θ. The scattering of light by larger particles is shown in Fig. 13.21 (b). Therefore the intensity of scattered light differs depending on the observation angle θ. The larger is angle θ, the greater is the reduction in scattering intensity $\bar{R}_{(\theta)}$. The factor by which the scattering intensity $\bar{R}_{(\theta)}$ (for a perpendicularly polarized incident beam diminished by interference) is diminished by interference at an angle θ is called the scattering function $P_{(\theta)}$ [where $\bar{R}_{(0)}$ equals the scattered light in the immediate vicinity of the primary beam, i.e. with θ→0]. Therefore, for the scattering intensity $R_{(\theta)}$ reduced to standard conditions and measured at the angle θ, one can write

$$\bar{R}_{(\theta)} = \bar{R}_{(0)} P_{(\theta)}$$

For larger molecules, scattering factor must be introduced into Debye equation (13.113)

$$\frac{Kc}{\bar{R}_{(\theta)}} = \frac{1}{P_{(\theta)}}\left(\frac{1}{M} + 2A_2c + \dots\right) \tag{13.114}$$

As the macromolecules are prudent in coil form in solutions, so the scattering factor $P_{(\theta)}$ would be dependent upon the scattering angle θ, the wavelength λ and the average coil radius $\bar{s}^2$. The following approximations has been written by Zimm as

$$\frac{1}{P_{(\theta)}} = 1 + \left(\frac{16\pi^2}{3\lambda^2}\right)\bar{s}^2 \sin^2\left(\frac{\theta}{2}\right)$$

Here $\bar{s}^2$ is gyration radius which is the average distance from axis of rotation at which all the masses could be concentrated to produce the same amount of moment of inertia that the actual distribution of mass possess.

$$\bar{s}^2 = \frac{4\pi}{\lambda}\sin\frac{\theta}{2}$$

Substituting the value of $1/P_{(\theta)}$ into equation (13.114), we get

$$\frac{Kc}{\bar{R}_{(\theta)}} = \left(\frac{1}{M} + 2A_2c + \dots\right)\left(1 + \left(\frac{16\pi^2}{3\lambda^2}\right)\bar{s}^2 \sin^2\left(\frac{\theta}{2}\right)\right) \tag{13.115}$$

Equation (13.115) has two variables c and θ, thus extrapolations can be made by varying one and kept the other constant and vice versa (Zimm plot Fig. 13.22). These extrapolations will help to get useful results.

(I) In the limit of c→0, equation (13.115) becomes

$$\left(\frac{Kc}{\bar{R}_{(\theta)}}\right)_{c\to 0}=\left(\frac{1}{M}\right)\left(1+\left(\frac{16\pi^2}{3\lambda^2}\right)\bar{s}^2\sin^2\left(\frac{\theta}{2}\right)\right)$$

The plot of $Kc/\bar{R}_{(\theta)}$ at c→0 versus $\sin^2(\theta/2)$ would yield a straight line with slope and intercept as

$$\text{Slope}=\frac{1}{M}\left(\frac{16\pi^2}{3\lambda^2}\right)\bar{s}^2$$

$$\text{Intercept}=\frac{1}{M}$$

Reciprocal of intercept gives value of molecular weight of polymer.

On dividing the slope with intercept, we get

$$\left(\frac{\text{Slope}}{\text{Intercept}}\right)_{c\to 0}=\frac{1}{M}\left(\frac{16\pi^2}{3\lambda^2}\right)\bar{s}^2(M)$$

$$\bar{s}^2=\left(\frac{\text{Slope}}{\text{Intercept}}\right)_{c\to 0}\frac{3\lambda^2}{16\pi^2}$$

In this way ratio of slope to intercept when c→0 gives value of gyration radius of polymer coil.

(II) Zimm plot (Fig 13.22) is the representation of light scattering data which can be used to conduct the following extrapolations of equation (13.115) on a single graph. In Zimm plot $Kc/\bar{R}_{(\theta)}$ is plotted against $\sin^2(\theta/2)+kc$. k is a constant which is chosen to give a good display to graph.

In the limit c→0 and θ→0°, then equation (13.115) becomes

$$\left(\frac{Kc}{\bar{R}_{(\theta)}}\right)_{c\to 0,\theta\to 0^\circ}=\left(\frac{1}{M}\right) \qquad (13.116)$$

In the limit c→0 , then equation (13.115) becomes

$$\left(\frac{Kc}{\bar{R}_{(\theta)}}\right)_{c\to 0}=\left(\frac{1}{M}\right)\left(1+\left(\frac{16\pi^2}{3\lambda^2}\right)\bar{s}^2\sin^2\left(\frac{\theta}{2}\right)\right) \qquad (13.117)$$

In the limit θ→0° , then equation (13.115) becomes

$$\left(\frac{Kc}{\bar{R}_{(\theta)}}\right)_{\theta\to 0^\circ}=\frac{1}{M}+2A_2c \qquad (13.118)$$

Value of M, A_2 and $\bar{s}^2$ can be obtained from extrapolated data of equation (13.116) to (13.118).

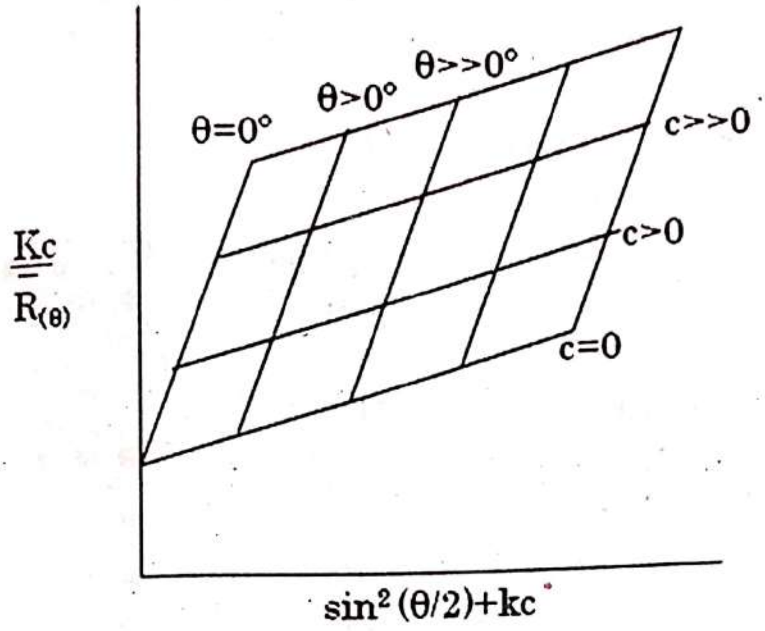


Fig. 13.22 Zimm plot in which $Kc/\bar{R}_{(\theta)}$ is plotted versus $\sin^2(\theta/2) + kc$

Table 13.1 Applicable weight range and average molecular weights determined from different methods

Method	Average	Applicable weight range
End group analysis	$\overline{M}_n$	upto 20,000
Membrane osmometry	$\overline{M}_n$	20,000 to 20,000,00
Vapour phase osmometry	$\overline{M}_n$	upto 40,000
Cryoscopy	$\overline{M}_n$	upto 40,000
Light scattering	$\overline{M}_w$	upto 50,000
Sedimentation	$\overline{M}_z$	upto ∞

13.9 ANALYTICAL METHODS

Molecular weight distribution determination method is analytical method. Centrifugation, turbidimetry, gradient elution and gel permeation chromatography (GPC) are analytical methods. Among analytical methods, GPC is most reliable and gives detailed and accurate analysis.

13.9.1 Gel Permeation Chromatography

Relative movement of polydisperse polymer solution is studied through chromatographic tank and analysis is done in GPC. It is the most accurate technique. It is used for fractionating polymer samples and measurement of molecular weight of every fraction. The fractionation is done with the help of a chromatographic tank filled with gel. And molecular weight of every fraction is determined with the help of refractometer connected with GPC.

Principle and Working of GPC

GPC is done with the help of a chromatographic tank filled with beads or gel as packing material. Then dilute solution of polymer is run through this tank with the help of pure solvent. As the solvent flows through column then polymer molecules move down and penetrate into gel spaces according to their size. Large molecules cannot penetrate easily as compared to smaller one. So fraction of molecules of higher weight moved down rapidly and collected first while fraction of molecules of smaller weights is collected later. By controlling crosslinking of gel, pore size is controlled. Thus by controlling pore size, we can limit size and weight of polymer collected in the end by GPC. From Fig 13.23 it is clear that small molecules penetrate into gel beads quickly while large molecules straightly moved down due to solvent flow.

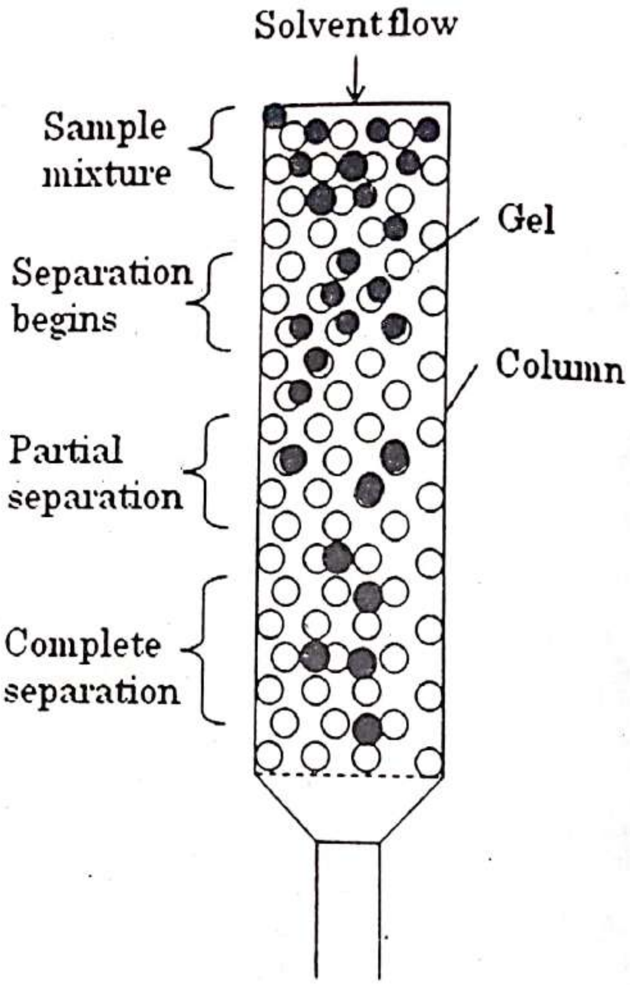


Fig. 13.23 The working of a simple GPC column

This method can be used for variety of polymers and solvents. When polystyrene gels are used, non-polar polymers can be analyzed using non-polar solvents like tetrahydrofuran. While polar gels are used for fractionation of polar polymers.

Determination of Molecular Weight

GPC is connected to a highly efficient computerized system. Refractive index of every fraction is different from that of other fraction. Computer determines refractive index of every fraction and volume of that fraction is calculated till refractive index does not change. Then computer plotted as spike as signal and gives value of molecular weight. In this way, molecular weight of every fraction and number of fractions are determined.

Q.20. If degree of polymerization of polystyrene is 16, then calculate molecular weight of polymer. (1664 g/mol)

Q.21. If degree of polymerization of nylon-6,6 is 402, then calculate its molecular weight. (90870 g/mol)

Q.22. If reactivity ratios of both monomers of a copolymer are equal, while their feed ratio is $[M_1] = 2\,[M_2]$, then calculate composition of copolymer.

$$\left(\frac{d[M_1]}{d[M_2]} = \frac{2(2r+1)}{r+2}\right)$$

Q.23. Using 0.2 as value of f_1, calculate values of F_1 and F_1. Remember r_1 is 0.28 and r_2 is 1.2. (0.308 and 0.7)

Q.24. A mixture of a polymer is given in the following table in the form of number of moles and molar mass distribution.

N_i (moles)	0.11	0.21	0.3	0.4	0.25	0.15
M_i (g/mol)	1	2	2.5	2.6	2.7	2.8

Calculate the following $\overline{M_n}$, $\overline{M_m}$ and $\overline{M_z}$.

Q.25. What is glass transition temperature? How can you determine value of T_g of a polymer experimentally.

Q.26. Calculate the number average degree of polymerization for a monomer conversion of 92%and 96% using Carothers's equation for the reaction of one mole of adipic acid with one mole of hexamethylenediamine to produce Nylon-6, 6.

REFERENCES

1. Painter, P. P. and M. M. Coleman, 1994. Fundamentals of Polymer Science: An Introductory Text, A Technomic Publishing Company, Pensylvania, USA.
2. More, W. R. 1967. An Introduction to Polymer Chemistry, University of London Press Ltd. UK.
3. Billmeyer, F. W. 1962. Textbook of Polymer Science, Interscience Publishers, Inc. New York.
4. Flory, P. 1953. Principles of Polymer Chemistry, Cornell University Press, Ithaca, New York.
5. Barrow, G.M. 1997. Physical Chemistry, GcGraw-Hill, Tokyo.
6. Bovey.F. A and F. H. Winslow, 1979. Macromolecules, Academic Press, New York.
7. Mark and Tobolsky, 1950. Physical Chemistry of High Polymeric Systems, Interscience Publishers, Inc. New York.
8. Misra, G. S. 2002. Introductory Polymer Chemistry, New Age International (P) Limited Publishers, India.
9. Levine, I.N. 2005. Physical Chemistry, Total McGraw-Hill Eduction Pvt Ltd., New Delhi, India.

QUESTIONS

Q.1. Identify synthetic and natural polymers from following list.

(a) Cellulose, (b) Orlon, (c) Polystyrene, (d) Starch, (e) Deoxyribonucleic acid, (f) Hemicellulose, (g) Polyaniline, (h) Polyvinyl chloride. (Natural: a, d, e and f, and synthetic: b, c, g, and h)

Q.2. Explain difference in structure of alternate, block, graft and random copolymers.

Q.3. Using diphenyl picryl hydrazyl as a free-radical initiator, write scheme of polymerization of propylene and iso-butylene.

Q.4. Suggest conditions under which copolymerization process is random, alternate and ideal.

Q.5. Explain why number average molecular weight is determined by osmometry, why not mass average?

Q.6. Suggest a method which gives detailed molecular weight distribution of a polydisperse sample without its fractionation.

Q.7. How does structure of a homopolymer is different from copolymer, explain under perspective of polymer of sulphur and nylon-6,6.

Q.8. What is the significance of molecular mass distribution in polymers? Discuss the different types of averages with respect to molecular mass distribution. Write a detailed account of viscometry in polymer characterization.

Q.9. Write a brief note on copolymerization.

Q.10. What are copolymers and why they are synthesize. Discuss kinetics of copolymerization. How do monomer reactivity ratios affect properties of copolymer.

Q.11. Write a brief note on molecular mass distribution.

Q.12. Write a brief account of different types of polymerizations.

Q.13. Give a mechanism of thermally catalyzed polymerizations and derive kinetic expression for it.

Q.14. What are addition polymers. What are different types of addition polymerizations. Derive kinetic expression for free radical chain polymerization.

Q.15. Explain condensation polymerization

Q.16. Describe method for determination of molar mass by osmometry

Q.17. Explain difference between condensation and addition polymerization with examples.

Q.18. Give detailed classification of polymers.

Q.19. Sample A and B of a polymer is polydisperse. 5, 3 and 2 chains of sample A have weight 9,000, 13,000 and 1,000 gmol^{-1} respectively. 6, 1 and 4 chains of sample B have weight 4,500, 1,000 and 15,000 g/mol respectively. Calculate $\overline{M}_n$, $\overline{M}_m$ and $\overline{M}_z$ of both samples. Compare values of $\overline{M}_n$, $\overline{M}_m$ and $\overline{M}_z$ of sample A with that of sample B. (Sample A: 8.6×10^3, 10.627×10^3 and 11.201×10^3 g/mol, and Sample B: 8×10^3, 11.619×10^3 and 13.73×10^3 g/mole)

Appendix A

SI UNITS AND CONVERSION FACTORS

Units form an integral part of any measurement. The numerical values of different properties of substances obtained as a result of experimental investigation can be expressed in different units. Chemists have traditionally used the metric system in all the measurements. It is simple and scientific. In this system all larger and smaller version of each basic unit could be obtained by multiplying or dividing the unit by 10. It is a decimal system or a base-10 system. In October 1960, the General Conference on Weights and Measures made an extensive revision of the metric system and adopted a new system of units called "*Le Systeme International d'Unit* (International System of Units)" to report scientific facts. Its purpose is to bring uniformity of style and terminology in communicating measurements.

The SI units are based on the seven base units given in Table A-1. Besides the base units, the principal derived units used in chemistry are given in Table A-2. Table A-3 gives the prefixes for fractions.

Table A-1. Base Units

Quantity	**Unit**	**Symbol**	**Definition**
Length	metre	M	The metre is the length of path travelled by light in vacuum during a time interval of $\frac{1}{299,792,458}$ of a second.
Mass	kilogram	Kg	The mass of the international prototype of the kilogram, a piece of platinum iridium alloy kept in Severes France.
Time	second	S	It is equal to the duration of 9192631770 cycles of the radiation associated with a specific transition of cesium-133 atom.
Electric current	ampere	A	The current that produces a force of 2×10^{-7} Nm^{-1} of length between two infinitely long, negligibly thick parallel conductors 1 metre apart in a vacuum.
Temperature	kelvin	K	The fraction $\frac{1}{273.16}$ of the thermodynamic temperature of the triple point of water.

Quantity	**Unit**	**Symbol**	**Definition**
Amount of substance	mole	Mol	The amount of substances of a system containing as many specified elementary entities (atoms, molecules, ions, etc.) as there are atoms in 0.012 kg of carbon-12.
Luminous intensity	candela	Cd	The perpendicular luminous intensity of a surface of $\frac{1}{600000}$ m^2 of a black body at the freezing point of platinum under a pressure of 101325 Nm^{-2}.

Table A-2. Derived Units

Quantity	**Unit**	**Symbol**	**Definition**
Force	Newton	N	$kg\ m\ s^{-2}$
Energy, work, quantity of heat	Joule	J	Nm (= $kg\ m^2\ s^{-2}$)
Power	Watt	W	$J\ s^{-1}$
Pressure	Pascal	Pa	$N\ m^{-2}$
Electric charge	coulomb	C	A s
Frequency	Hertz	Hz	s^{-1}
Electrical potential difference	Volt	V	$J\ A^{-1}\ s^{-1}$ (= JC^{-1})
Resistance	Ohm	Ω	$V\ A^{-1}$
Conductance	Siemen	S	Ω^{-1}
Capacitance	Farad	F	$A\ s\ V^{-1}$ (= C/V)

Table A-3. Prefixes

Fraction	**Prefix**	**Symbol**	**Fraction**	**Prefix**	**Symbol**
10^{-1}	deci	D	10	deca	da
10^{-2}	centi	C	10^2	hecto	h
10^{-3}	milli	M	10^3	kilo	k
10^{-6}	micro	μ	10^6	mega	M
10^{-9}	nano	N	10^9	giga	G
10^{-12}	pico	P	10^{12}	tera	T
10^{-15}	femto	F	10^{15}	peta	P

USEFUL CONVERSION FACTORS

1 angstrom (Å) = 10^{-8} cm = 0.1 nm = 10^{-10} m

1 atm = 760 mm Hg = 760 torr = 1.01325×10^{6} dyn cm^{-2} = 101,325 N m^{-2}

1 bar = 10^{6} dyn cm^{-2} = 0.987 atm = 100,007.8 Nm^{-2} = 10^{-5} Nm^{-2}

1 cal = 4.184 J = 4.184×10^{7} ergs

1 coulomb = 2.9979×10^{9} esu

1 dyn = 10^{-5} N

1 erg = 2.39×10^{-8} cal = 10^{-7} J

1 eV = 23.06 k cal mol^{-1} = 1.602×10^{-12} erg = 1.602×10^{-19} J

1 F = 96,487 coulomb $equiv^{-1}$

1 R = 8.314 J K^{-1} mol^{-1} = 1.987 cal^{-1} K^{-1} mol^{-1} = 0.08205 litre atm K^{-1} mol^{-1}

1 esu = 3.334×10^{-10} C

1 cm^{-1} (wave number) = 1.986×10^{-23} J

1 litre = 10^{-3} m^{3}

1 inch = 0.0254 m = 2.54 cm

1 mile = 1609 m

1 foot = 0.3084 m

1 poise = 10^{-1} kg m^{-1} s^{-1}

1 dyn cm^{-1} = 10^{-3} N m^{-1}

Appendix B

SI VALUES OF SOME FUNDAMENTAL CONSTANTS

Quantity	**CGS units**	**SI units**
Avogadro's number (N_A)	6.0225×10^{23}	6.0225×10^{23}
Boltzmann's constant (k)	1.3805×10^{-16} erg K^{-1}	1.3805×10^{-23} J K^{-1}
Electron charge (e)	4.803×10^{-10} esu	1.602×10^{-19} C
Electron mass (m_e)	9.1096×10^{-28} g	9.1096×10^{-31} kg
Faraday constant (F)	96,487 coulombs g $equiv^{-1}$	96,487 C mol^{-1}
Gas constant (R)	8.314×10^{7} ergs K^{-1} mol^{-1}	8.314 J K^{-1} mol^{-1}
Planck's constant (h)	6.6256×10^{-27} erg s	6.6256×10^{-34} J s
Proton mass (m_p)	1.6725×10^{-24} g	1.6725×10^{-27} kg
Rydberg constant (R_H)	1.09737 cm^{-1}	1.09737×10^{7} m^{-1}
Speed of light in vacuum (c)	2.99795×10^{10} cm s^{-1}	2.99795×10^{8} m s^{-1}

Appendix C

GREEK ALPHABETS

Alpha	A	α
Beta	B	β
Gamma	Γ	γ
Delta	Δ	δ
Epsilon	E	ε
Theta	Θ	θ
Zeta	Z	ζ
Eta	H	η
Iota	I	*I*
Kappa	K	κ
Lambda	Λ	λ
Mu	M	μ
Nu	N	ν
Xi		ξ
Pi	Π	π
Rho	P	ρ
Phi	Φ	ϕ
Psi	Ψ	ψ
Omega	Ω	ω

Appendix D

MATHEMATICAL FORMULAE

Exponents and Powers

* $1 = 10^0$
* $0.1 = 10^{-1}$
* $1000 = 10^3$
* $a^x \times a^y = a^{x+y}$
* $\frac{a^x}{a^y} = a^{x-y}$
* $(a^x)^y = a^{x \times y}$
* $a^0 = 1$

Logarithem

* $\log xy = \log x + \log y$
* $\log \frac{x}{y} = \log x - \log y$
* $\log a^x = x \log a$

Equations

(i) Linear equations

	Equation	Type	Slope	Intercept
*	$y = mx$	Straight line passing through origin	m	0
*	$y = -mx$	Straight line passing through origin	$-m$	0
*	$y = mx + c$	Straight line with intercept form	m	c
*	$y = -mx + c$	Straight line with intercept form	$-m$	c

(ii) Quadratic Equation

$$y = ax^2 + bx + c$$

To find value of x, $x = \dfrac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

and $x \neq 0$

(iii) Differentiation

*	$\dfrac{d}{dx}c = 0$, where c is constant	*	$\dfrac{d}{dx}\cos x = -\sin x$
*	$\dfrac{d}{dx}x^m = mx^{m-1}$	*	$\dfrac{d}{dx}a^x = a^x \ln a$
*	$\dfrac{d}{dx}x = 1$	*	$\dfrac{d}{dx}e^x = e^x$
*	$\dfrac{d}{dx}\sin x = \cos x$	*	$\dfrac{d}{dx}\ln x = \dfrac{1}{x}$

(iv) Integration

	$\int x^m dx = \dfrac{x^{m+1}}{m+1}$	*	$\int (ax+b)^m dx = \dfrac{(ax+b)^{m+1}}{a(m+1)}$
*	$\int \dfrac{1}{x} dx = \ln\|x\|$	*	$\int e^x dx = e^x$
*	$\int e^{(ax+b)} dx = \dfrac{e^{(ax+b)}}{a}$	*	$\int \sin x dx = -\cos x$
*	$\int \cos x dx = \sin x$		

Caravan

Books on Chemistry

TEST YOUR CHEMISTRY

By

Prof. Dr. Haq Nawaz Bhatti

This book is written for undergraduates and postgraduate students of chemistry and allied fields with the intention that they could show better performance during various examinations and interview held for academic purposes. The information has been categorized under several headings. This is a question-answer type book and covers all fundamentals as well as postgraduate level queries, probes and questions.

PRINCIPLES OF PHYSICAL CHEMISTRY

By

Prof. Dr. Haq Nawaz Bhatti

This book on Physical Chemistry is written for B.Sc (Pass) and BS students for all Universities of Pakistan according to revised curriculum developed by Higher Education Commission, of Pakistan. The book has been written in a clear and lucid language. The book contains considerable number of worked out examples exposing the students to practical applications of equations and helping them comprehend the magnitude of different physiochemical quantities.

MODERN INORGANIC CHEMISTRY

By

Prof. Dr. Haq Nawaz Bhatti

This book on Inorganic Chemistry is written for B.Sc (Pass) and BS students according to revised curriculum developed by Higher Education Commission, of Pakistan. Simple and lucid language has been used to express the subject matter. The book is presented beautifully in different chapters for convenience of the readers. The book is quite up to the mark with the latest approach and true to the standard of various examinations

ORGANIC CHEMISTRY

By

K M Ibne Rasa, Abdur Rahman

This book on Organic Chemistry is written for B.Sc (Pass) and BS students according to revised curriculum developed by Higher Education Commission, of Pakistan. Simple and lucid language has been used to express the subject matter. The book is presented beautifully in different chapters for convenience of the readers. A study of this book will help the students not only to understand to material presented but will develop their ability to reason and to think.

Caravan Book House - Lahore